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# TEACH YOURSELF CHEMISTRY

A PRACTICAL BOOK OF SELF-INSTRUCTION IN  
CHEMISTRY, BASED ON THE WORK BY JAMES  
KNIGHT, M.A., [B.Sc., COMPLETELY REVISED AND  
ENLARGED BY

G. BRUCE MACALPINE, B.Sc.



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## PREFACE TO THE SECOND EDITION

IN offering the Second Edition of "Teach Yourself Chemistry," opportunity has been taken to overhaul the text thoroughly and to add to it six specially-written chapters of completely fresh matter.

It will be noticed that a good deal of attention has been paid to what is frequently called Organic Chemistry. No apology is offered (except to the printer) for the introduction of numerous chemical formulæ, since the present writer believes that those who are interested enough to wish to read such a book as this will expect to find such things in it.

It is hoped that the information contained in this book may prove of some assistance in introducing readers to a more serious study of chemistry. There are many excellent text-books for those wishing to learn more of the theory of the subject, and the services of the local Public Library should be enlisted in this connection. The chemist, however, is essentially a practical worker, and instruction in practical chemistry is only to be had in the laboratories of schools, technical colleges, and universities.

In compiling the present work, many books, large and small, were consulted. In particular, much of the information in Chapter XVII was derived from a booklet "The Vitamins, an Epitome of Contemporary Knowledge", published by The Crookes Laboratories (British Colloids, Ltd.), to whom grateful thanks are tendered.

G. B. M.





## INTRODUCTION

THIS book is intended for all who wish to keep abreast of their daily reading and daily tasks, and who, by reason of a one-sided system of culture in youth, have felt themselves in matters relating to the outside world as the stranger within or even outside the gates. For these this chemistry of daily life may well serve as an introduction to the more systematic study of the science, and those who take the trouble to work, not merely read, through the following pages will be agreeably surprised to find to what numerous and varied applications their acquirements may be put.

Since it is desirable that the study of chemistry, even in an elementary way, should be as practical as possible, a few hints on the manipulation and choice of apparatus may not be out of place.

One of the first duties of a practical student is to fit up a flask with cork and delivery tubing. Corks should always be chosen a size too large and then pressed or rolled under the foot till small enough. A cork should always be screwed in rather than pushed, and in extracting, the screw should be continued and in the same direction, not reversing the spiral as with a corkscrew. Holes require a cork-borer a size smaller than the tube to be used; the opening is widened and smoothed by a rat-tail file and the tube screwed into position. Where gas is to be collected, especially with such a light diffusible gas as hydrogen, corks are too porous, and indiarubber stoppers must be used; these are to be obtained to order solid or with one or two holes.

Glass tubing is of two kinds—soft glass for delivery tubes and general connections, and hard glass for combustion work. The soft glass tubing is usually of  $\frac{1}{4}$ -in. diameter, and about a yard of it may be cut up into

short lengths for making right-angled bends, of shapes  and , while one or two pieces may be kept a foot long. Soft glass is easily cut by laying it on a table and making a scratch all round with a three-cornered file; the tube is then broken as one would break a wooden match. The sharp edges left in this way interfere with the use of corks, so that they have to be rounded by holding the tube above a gas flame till the glass partly melts. Hard glass tubing for combustion

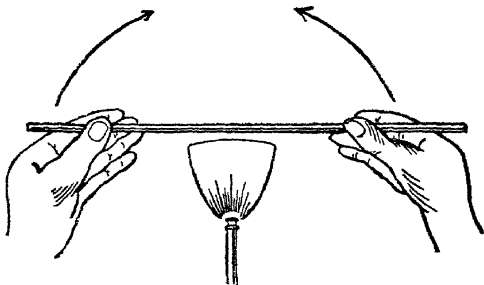


FIG. 1.

experiments should be about  $\frac{5}{8}$  in. in diameter; it is generally thicker and harder, and requires more work with the file. The edges need not be rounded, since in this case it is the cork that is usually fitted into the tube.

In bending soft tubing the tube should be held in both hands, palms up, just above the edge of an ordinary flat gas flame (see Fig. 1). A bunsen flame is of no use in bending tubes, since too small a part is heated and the bent tube is far too much constricted at that point. When the glass gets soft, remove it from the flame and bend the tube to the required angle, holding it in that position till the glass hardens, then round off the edges as usual.

Sometimes a tube has to be widened, narrowed, or

closed together. To widen a tube hold it obliquely with one end just above and finally in the bunsen flame, revolving the tube between the fingers and thumb. When the mouth of the tube softens, remove it from the flame and screw into it any conical mould, such as a charcoal pencil, a common lead pencil or even a boy's top if the metal be previously warmed. In order to narrow a tube, as in making a jet for hydrogen gas, heat it as if in bending, rolling the tube between the finger and thumb to heat the glass uniformly. When the centre softens, remove it from the flame and, while still slowly revolving, pull the ends gently apart till the desired taper is produced. When the glass is cold, cut it with a file at the narrowest part. A gentle taper is produced by moderate heat and a gentle pull; if the glass be held long in the flame and pulled apart smartly, the result is a long tail of glass which closes the tube altogether. Most of this may be snapped off, leaving a small opening which closes on further heating. To avoid thickening at the closed end it is better to remove the glass while soft and blow gently into the tube till the thickness is uniform; by further blowing a thin bulb may be obtained.

Flasks should always be supported on wire gauze, and the flame should always be directed on the portion filled with liquid, never at the edge of the liquid. If solids are to be heated in a glass vessel, as when sal-ammoniac and lime are heated together in making ammonia, the vessel should always be kept moving, being held in the hand preferably above a moderate flame. In experiments where a gas is being evolved and collected over water—*e.g.*, in making oxygen—the gas comes off with such a rush towards the end that it is advisable to withdraw the burner for a moment or two. In such cases, when a sufficient supply of gas has been obtained, all connection with the water-trough should be cut off, either by lifting out the delivery tube, by slipping off the indiarubber connections, or by with-

drawing the cork of the flask, since otherwise water will rush back into the heated flask, cracking the glass and probably exploding it owing to the sudden generation of steam.

Evaporation of solutions is carried out in small basins of porcelain or enamelled iron, supported on a tripod or ring-stand. To prevent loss by boiling over, the basin should not be more than half-filled, and since the expulsion of the last drops of water is usually accompanied by considerable sputtering, the operator should remove the burner and "stand by". Should it be necessary to convert the residue into oxide, as in estimating the amount of "ash" in foods, soils, etc., a platinum capsule is required so that the contents may be maintained at a red heat for some time.

Filtering is another operation which only needs to be seen once. The filters are squares or circles of unsized paper like thin white blotting-paper, and the circle is first folded upon its diameter, then into a quadrant, finally opened out as a paper cone with three plies of paper on one side and one on the other. The cone is now placed in a glass funnel at least an inch larger; it is then moistened with water, and is now ready for use.

In pouring a muddy liquid into such a filter some time will be saved by decanting—*i.e.*, allowing most of the sediment to settle—and pouring the upper and clearer liquid on to the paper. This allows most of the liquid to run through fast before the pores of the filter get clogged. A warm solution always filters more rapidly than a cold one. The solution should be poured gently on to the threefold side of the paper, and not directly into the bottom, but about half-way up. When a liquid is poured at once into the apex of the cone, the finer particles are often forced through by water-pressure, giving a muddy filtrate which requires to be sent through again. On the other hand, the liquid should not be allowed to rise within a third of an inch of the top, since it has always a tendency to creep over the edge of the

paper by capillary attraction, especially if the paper is not previously moistened. It is difficult to pour liquid into a filter from a full glass without spilling some; in this case a wet glass rod is held in the filter resting on the threefold paper, and the upper end is held against the glass so as to catch the stream of liquid (see Fig. 2). In

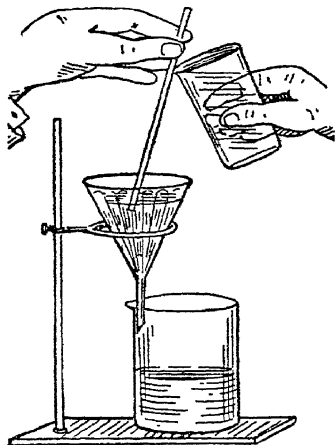


FIG. 2.

exact work the residue left on the filter-paper has to be washed with water so as to remove the last traces of liquid, the washings being added to the original filtrate.

Test-tubes are usually of three kinds—common test-tubes for general purposes, 6 in. by  $\frac{5}{8}$  in.; tall, narrow tubes 6 in. or 7 in. by  $\frac{1}{2}$  in. for heating small quantities of solids; and, lastly, “boiling-tubes”, which are large test-tubes 8 in. by 1 in., and used, as their name implies, for boiling rapidly small quantities of liquid. A test-tube which is being heated should be held at right angles



to the hand, as nearly horizontal as the contents will admit, and kept gently rolling between the fingers and thumb, the latter uppermost, and with the mouth of the tube to the right front of the operator. In this way a large heating surface is presented to the flame, and any sudden burst of steam or liquid spurts out clear of the person. If a tube gets too hot, owing to long boiling, it may be held in a strip of paper folded several times, or the handkerchief may be twisted at one corner and the rope used as a ring handle. In "dry testing", where small quantities of solids are heated to mark their behaviour as to colour changes, evolution of vapours, and so on, a long, narrow tube should be used, and a pinch of the substance dropped into the bottom. This alone is heated, the tube being held horizontally with its mouth closed by the thumb to secure any gases which may require examination. Broken test-tubes are not useless; in most cases only the bottom has been knocked off, and they do very well for dry testing, as also for experiments in closing tubes, bulb-blowing, and other useful manipulations. It is part of the training of every chemist to create as little waste as possible, and when he does, to utilise, if he cannot recover it.

When a student has learned these preliminary manipulations he may be safely trusted with a case of test-tubes and some beakers and flasks, and with ordinary care half-a-crown per annum should cover the cost of breakages and renewals. It is important to grasp firmly some standard notions of mass, whether as weight or bulk, and for this purpose a chemical balance and a measuring glass, say, of 200 cubic centimetres, are required. At a later stage he will try some experiments which call for a little more care, such as those involving explosions and the use of electric apparatus, and in these cases trials should always be made with small quantities till confidence is established.

For the sake of some who may be disposed to do a little at home, say, to verify all the experiments in this

book, a list of useful apparatus is appended, although a "handy man" need never be at a loss for a pneumatic trough while a tumbler and saucer may be had.

Test-tube stand to hold 1 doz. small and 2 large tubes.  
1 doz test-tubes, 6 in by  $\frac{3}{8}$  in.  
 $\frac{1}{2}$  doz. boiling-tubes, 8 in by 1 in.  
Tripod-stand.  
Tongs  
2 evaporating basins, enamelled iron, 4 in.  
Retort stand with 3 rings and screw clamp.  
2 filter funnels.  
Blowpipe.  
2 Bunsen burners, medium size.  
Bunsen tubing for above  
(Where gas is not available two spirit lamps may be used.)  
6 20-oz flasks.  
1 doz. flasks, 12 to 16 oz.  
Set of 3 beakers.  
Beehive shelf.  
Woulff bottle, 2 necks, with indiarubber stoppers.  
2 Thistle funnels.  
Wire gauze, 2 squares.  
Glass tubing, 3 ft. combustion tubing,  $\frac{1}{8}$  in. to  $\frac{3}{8}$  in.  
" 3 ft. soft tubing,  $\frac{1}{4}$  in. for connections.  
Wide-necked bottles, to be used as gas jars.  
3 ft indiarubber tubing,  $\frac{3}{8}$  in. or  $\frac{1}{4}$  in., for connections.  
2 porcelain crucibles,  $1\frac{1}{2}$  in.  
2 fireclay crucibles.  
Charcoal block.  
Filter-paper.  
Book of litmus paper, mixed.  
Triangular saw file.  
Thermometer, to 200° C.  
Liebig's condenser, 18 in.  
Chemical balance; weights, 50 to 0.001 gram.

The few chemicals which are required in the solid state are best purchased in small quantities—say four ounces at a time—and kept in stoppered, wide-mouthed bottles. Deliquescent solids, like calcium chloride, as well as substances like caustic soda and potash, which are affected by the air, should be kept tightly corked. It is not advisable to keep soda and potash in bottles with glass stoppers, unless these have been smeared with vaseline, since the alkali often renders the stoppers quite fast. Liquids should be kept in the ordinary

eight-ounce bench-bottles, and be marked preferably with varnished labels; bottles containing strong alkaline solutions should have their stoppers smeared as above or else provided with rubber stoppers. A liquid like ammonia, which is of frequent domestic application, should be purchased in concentrated form and of specific gravity 0.880. This solution should be kept in a cool place with the stopper smeared; and where it is likely to be much in use a Winchester may be filled with a 10 per cent. solution—*i.e.*, one part of the strong ammonia to nine parts of water. Lime-water is another liquid much in demand; it is easily made by shaking up a piece of fresh lime the size of a walnut in a Winchester quart of water. From this stock solution a small bench-bottle may be replenished. The only other liquid which may be used in large quantities is sulphuric acid; for most purposes the commercial acid is quite strong enough, and for battery purposes or for making sulphuretted hydrogen or hydrogen itself one part of this in eight to twelve parts of water will be found suitable. Yellow phosphorus should, of course, be kept and handled under water, while ether and carbon disulphide should be kept in glass-stoppered bottles, used in small quantities at a time, and never brought near a flame, since they are both very volatile and very inflammable. A few crystals of iodine may be kept solid, but this substance is generally used in solution, either in water or spirits of wine.

Detailed lists of apparatus are easily procurable from the different dealers in scientific fittings, but the ordinary layman, who wishes simply to verify what he has been reading, will find that a few tubes and flasks to stand heat, supplemented by an odd tumbler or plate from the pantry, will be apparatus enough to repeat some of the most striking and instructive experiments of Davy or Faraday. A good workman creates tools when required; a bad workman first spoils them and then complains of them.

# CONTENTS

CHAP.	PAGE
INTRODUCTION . . . . .	vii
I. THE ATOMIC THEORY . . . . .	17
II. CHEMICAL NOMENCLATURE . . . . .	28
III. CHARACTERS OF CHEMICAL ACTION . . . . .	44
IV. WATER . . . . .	51
V. THE ATMOSPHERE . . . . .	59
VI. OXIDATION AND COMBUSTION . . . . .	66
VII. CARBON AND ITS OXIDES . . . . .	73
VIII. THE DISTILLATION OF COAL . . . . .	89
IX. SULPHUR AND CHLORINE . . . . .	97
X. NITROGEN AND PHOSPHORUS . . . . .	110
XI. CHEMISTRY OF THE ROCKS . . . . .	117
XII. IRON AND OTHER METALS . . . . .	124
XIII. CARBON AND ITS COMPOUNDS . . . . .	138
XIV. SYNTHETIC PRODUCTS . . . . .	159
XV. FOOD . . . . .	172
XVI. DIGESTION AND RESPIRATION . . . . .	188
XVII. THE VITAMINS . . . . .	197
XVIII. CHEMISTRY OF PHOTOGRAPHY . . . . .	210
XIX. CLASSIFICATION OF THE ELEMENTS . . . . .	226
INDEX . . . . .	237

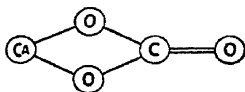


## CHAPTER I

### THE ATOMIC THEORY

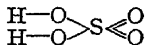
MATTER, as distinguished from Mind, is characterised by certain properties; thus it occupies space, it may be made to occupy less space, it is penetrable, divisible, possesses weight, and so on. When a lump of chalk is broken up into smaller lumps, each of these is still chalk, and possesses all the properties of matter due to chalk, except, of course, those connected with loss of size. Let a small piece of chalk be very finely powdered; the result is a very fine dust, the separate particles of which may be almost invisible, but each particle is still a particle of chalk: its nature as a kind of matter is unchanged. Matter thus seems to be infinitely divisible, and as a matter of fact such divisibility has been carried a very long way. A single grain of gold may be beaten out so as to give a square of gold leaf measuring 7 inches each way; this square may be ruled into thin strips of 100 to the inch, and these again cross-divided, so as to give 490,000 visible pieces of gold, each the  $\frac{1}{100}$ th of an inch square. If, however, the gold leaf be attached to a sheet of glass, the cross-ruling may be made very much finer, for 10,000 parallel lines can be drawn by dividing machinery within a single inch, so that, by cross-ruling, a single grain of gold may be divided into 4,900,000,000 pieces, visible under a microscope, but each one still a piece of gold. In the case of solutions, as when salt dissolves in water, the process of division is carried so far that not even the most powerful microscope can detect the particles of salt. In opposition, however, to the common view of the infinite divisibility of matter, chemists maintain that such division may be carried on up to a certain point only, and that the next attempt at division involves the destruction of the substance altogether by breaking it up into simpler bodies. Thus,

according to chemists, chalk yields nothing but chalk in finer and finer particles till we arrive at a molecule of chalk, the finest particle of chalk possible or conceivable; but if division be pushed beyond this, the molecule or ultimate particle of chalk is broken up into five separate atoms, one a metal called calcium, one a non-metallic solid called carbon, and three of oxygen gas. A molecule is thus the smallest possible quantity of any kind of matter—say, chalk—which can exist as such, and a molecule is built up of atoms, two or more, held together by various bonds, some being more loosely tied than others. In this way a molecule of chalk may be figured as a kind of compound atom thus :—



or, more simply,  $\text{Ca} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}=\text{O}$

in which five atoms of the elements calcium, carbon, and oxygen combine to form chalk or calcium carbonate, represented by the formula,  $\text{CaCO}_3$ . In the same way sulphuric acid or oil of vitriol may be divided to inconceivable, though not immeasurable, amounts by putting one drop of acid in 1,000 of water, then one drop of this solution into 1,000 of fresh water, and so on. But, says the chemist, there is a limit to all this, and you finally reach the smallest possible particle of sulphuric acid, the molecule figured thus :—



consisting of seven separate atoms, and any further attempt at division breaks up the acid altogether, giving simpler bodies such as  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ , depending

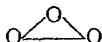
on how the division has been effected. Even in the case of a simple or elementary gas like hydrogen, the molecule or ultimate particle generally contains two atoms, thus :—



while the difference in strength and density of common oxygen and ozone is shown by the fact that the molecule of oxygen is figured as—

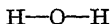


two atoms tightly held together, while that of ozone appears as—



three atoms loosely tied, and therefore more easily decomposed.

These molecules or ultimate particles of any given kind of matter must be inconceivably small, and Lord Kelvin calculated that if a drop of water were magnified up to a globe the size of our earth the molecules of water would then appear as bodies intermediate in size to cricket-balls and footballs, each molecule again being composed of three atoms—



While a molecule is the smallest possible particle of matter existing as such, an atom is smaller still, and may be defined, though not described, as the smallest portion of matter capable of entering into combination. An atom is therefore generally more active than a molecule, since the latter is the physical expression of a state of rest, the atoms having already made their combinations. If, however, a combination is broken up, the atoms are free to recombine, and the substances formed are said to be nascent, newly born. If a stream of hydrogen gas be bubbled through some ferric chloride in a glass, no change occurs in the brown colour of the liquid, but if a



piece of zinc be put in and sulphuric acid allowed to trickle down the glass and reach the zinc, the chemical equilibrium is disturbed and hydrogen gas is liberated within the liquid. This nascent hydrogen proves its greater power by attacking the ferric chloride and converting it into greenish ferrous chloride.

To a chemist, then, an element is a substance whose molecules consist of atoms of the same sort, as in oxygen and ozone, figured above; a compound is a substance whose molecule consists of two or more atoms of different sorts, like water, chalk, and sulphuric acid. Roughly speaking an element is any substance which has hitherto defied all attempts to break it up, but with the discovery of new methods of analysis it has been found that many elements are not as "elementary" as once was thought. Thus lime, soda, potash, and many other so-called elements, have been broken up by electric agency, yielding metals, calcium, sodium, and potassium, the existence of which had been suspected, but not proved.

These atoms are assumed to be comparable but not equal in size, and to differ in other physical properties, including weight. In estimating the weights of gases, pure dry hydrogen is taken as the standard of specific gravity, and in the case of solids and liquids, distilled water is the standard; thus the specific gravity of sulphuric acid is 1.842, meaning that a cubic inch or other volume of acid weighs 1.842 times as much as the same volume of water. Hydrogen gas is the lightest known substance, being less than  $\frac{1}{14}$ th of the weight of air, so chemists to begin with adopted hydrogen as their standard of weight, and all other elements were compared with hydrogen in giving their atomic weights. For various reasons, the practice now is to compare all the other elements with oxygen which is taken as 16 exactly; this means that the atomic weight of hydrogen is no longer unity but 1.008. The atomic weights of substances like copper and carbon, which are not gases at all, are got in a more roundabout fashion.

All bodies, generally speaking, expand when heated; and it can easily be shown experimentally that all gases, whether simple like oxygen, or compound like carbonic-acid gas, expand at the same rate—namely,  $\frac{1}{273}$  of their bulk for every degree centigrade. This uniformity of expansion leads to the conclusion that all gases have the same number of molecules (not atoms) per cubic inch, for only on that supposition could uniform expansion be possible, since expansion means increase of the space already existing between the molecules. This conclusion is known in chemistry as Avogadro's Law. In this way the density of a gas—*i.e.*, its weight compared with hydrogen—may be calculated from the atomic weight of its constituents in the molecule, remembering that the molecule of hydrogen is not H, but H<sub>2</sub>, thus:—



and so for all other elementary gases. For instance, the chemical symbol for carbon is C, and its atomic weight 12; that of oxygen is O, and its atomic weight 16. These combine to form carbonic-acid gas, having a formula CO<sub>2</sub>; what is the density of this gas? The atomic weights of one atom of carbon and two atoms of oxygen give 12 + 2 × 16, or 44 in all, which has to be compared with H<sub>2</sub> or 2; the required ratio is therefore 44 : 2 or 22 : 1—*i.e.*, carbonic-acid gas is 22 times as heavy as hydrogen.

Elements are denoted by symbols, generally the initial letter of their names, though in many cases the Latin name has been taken. Thus the symbol for iron is not I—which means iodine—but Fe, from the Latin *ferrum*; F alone would mean fluorine. In the same way potassium is symbolised by K for *kalium*, the root of the word alkali, while P is appropriated for phosphorus, and Na is the symbol for sodium, the old name for soda being

by urea  $\text{CO}(\text{NH}_2)_2$ , and ammonium cyanate  $(\text{NH}_4)\text{CNO}$ , both of which give as their empirical or analytical formula  $\text{CON}_2\text{H}_4$ . More will be found about the importance of these two compounds in advanced text-books; suffice it to say that one may easily be changed into the other by ordinary chemical methods.

Looking back to the graphic formula recently given for sulphuric acid, it will be seen that some atoms are connected by a single tie, some by two, and the sulphur atom by no fewer than six. These ties are intended to show the combining power or valency of the elements, and it will be observed that here also hydrogen is taken as the unit, since an atom of hydrogen has the lowest combining power of any element. Substances which resemble hydrogen in having but a single tie are called monads or univalent elements; oxygen is the type of a large class of substances capable of uniting with two atoms of hydrogen, and therefore called diads or divalent; carbon is a tetrad (quadrivalent), as shown by the formulæ  $\text{CH}_4$  and  $\text{CO}_2$ , for marsh gas and carbonic-acid gas respectively; while sulphur is a hexad, able to take three oxygen atoms, as in  $\text{SO}_3$  and in sulphuric acid.

The table on p. 25 exhibits the valency, or, as it is sometimes called, the combining power of the common elements: The valency of any substance may be got from an examination of its compounds, generally chlorides or oxides. Chlorine itself is a monad, as seen by hydrochloric acid—



barium chloride, however, is  $\text{BaCl}_2$ , and barium oxide  $\text{BaO}$ , showing that barium is a diad. In gold chloride, again, 197.2 parts, or one atom of gold ( $\text{Au}$ ), are found to combine with three times 35.5, or three atoms of chlorine, giving a formula  $\text{AuCl}_3$ , showing gold to be a triad. Marsh gas,  $\text{CH}_4$ , shows the valency of carbon; sal-ammoniac,  $\text{NH}_4\text{Cl}$ , shows the pentad nature of nitrogen;

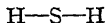
TABLE OF VALENCIES.

Monad.	Diad.	Triad.	Tetrad.	Pentad.	Hexad.
H	O	B	Cu	N	S
Li	Be	Al	Si	P	Cr
Na	Mg	Sc	Ti	V	Se
K	Ca	Ga	Sn	As	Mo
Cu	Zn	Au	Pb	Sb	Te
Rb	Sr	N	N	Bi	W
Ag	Cd	P	S	Cl	U
Cs	Ba	As	Pt	S	Mn
Au	Hg	Sb	C		
F	Sn	Fe	Cl		
Cl	Pb	Bi			
Br	Fe				
I	N				
N	Pt				
Hg	Cu				
	S				
	C				
	Mn				

while  $\text{SO}_3$ , sulphur trioxide, shows that an atom of sulphur may combine with three atoms of oxygen, which again are equivalent to six atoms of hydrogen or chlorine. The curious thing about valency is the variation shown within certain limits by common elements. Thus in sulphur trioxide,  $\text{SO}_3$ , sulphur is fully saturated with oxygen and behaves as a hexad, but in the dioxide,  $\text{SO}_2$ , it behaves as a tetrad, thus :—



while in sulphuretted hydrogen,  $\text{H}_2\text{S}$ , it appears as a diad only—



its other combining powers being unsaturated or in abeyance. In the same way nitrogen, the full valency of which is five, appears as a triad in ammonia,  $\text{NH}_3$ . Those substances, however, which have an even valency remain even, like sulphur, which shows 6, 4, 2, while those which are odd, like nitrogen, remain odd, 5, 3, 1,

and this is sought to be explained by saying that the unused ties combine with each other, thus :—



is hexad sulphur, as in—



$\begin{array}{c} \text{H} \\ | \\ \text{S} \\ | \\ \text{H} \end{array}$  is tetrad sulphur, as in  $\text{O}=\text{S}=\text{O}$

and  $\text{H}-\text{S}-\text{H}$  is diad sulphur, as in  $\text{H}-\text{S}-\text{H}$

This also helps to explain the fact that unsaturated compounds generally miss no opportunity of saturation; thus carbon monoxide, CO, burns readily into the fully-saturated dioxide, CO<sub>2</sub>, and sulphuretted hydrogen, H<sub>2</sub>S, passes naturally by oxidation into sulphurous acid, and finally into sulphuric acid, the fully-saturated form. The importance of a knowledge of valency will be more apparent when taken in connection with chemical nomenclature. All these remarks on atoms are, of course, like the atomic theory itself, pure theory or speculation. It may be true that matter is infinitely divisible after all, as metaphysicians claim; but one thing chemists may say, and say truly, namely, that the theory explains the phenomena. There can be no tangible or visible proof of the existence of atoms, or of their arrangement within a molecule, but it is true that matter arranged upon the line of the atomic theory would behave precisely as does the matter with which we are acquainted.

The efforts of modern physical investigators are gradually revealing the truth of theories about the existence and arrangement of atoms. Though they will never be seen, their existence and position may now be quite clearly demonstrated. Despite these advances, however, the answer to the question "What is an

atom? " is still shrouded in mystery, which seems to be more, instead of less, obscure despite our wider knowledge.

When a substance cannot be decomposed by any method at present known, it is called an *element*. Many substances formerly reckoned such have been decomposed on the discovery of new methods of analysis; thus lime and soda have yielded the metals calcium and sodium respectively, and it is to be understood that the term "element" is altogether provisional. Ninety such elements are at present (1945) known, the great majority being metals of no importance; only twenty-five are non-metals, and the commoner elements number only some two dozen in all. In the following table, which excludes the rarer elements, important substances are printed in small capitals, while the non-metals are marked with an asterisk, and metals are in italics.

A complete list of the known elements, with their atomic weights, is given on p. 236.

TABLE OF COMMON ELEMENTS, WITH THEIR CHEMICAL SYMBOLS AND ATOMIC WEIGHTS.

Name.	Sym.	At. wt.	Name.	Sym.	At. wt.
ALUMINIUM	Al	27	MAGNESIUM	Mg	24
<i>Antimony</i> (Stibium)	Sb	122	MANGANESE	Mn	55
<i>Arsenic</i>	As	75	MERCURY (Hydargyrum)	Hg	200
<i>Bismuth</i>	Bi	209	NICKEL	Ni	58
* <i>Boron</i>	B	11	*NITROGEN	N	14
*BROMINE	Br	80	*OXYGEN	O	16
<i>Cadmium</i>	Cd	112	*PHOSPHORUS	P	31
CALCIUM	Ca	40	<i>Platinum</i>	Pt	195
*CARBON	C	12	POTASSIUM (Kalium)	K	39
*CHLORINE	Cl	35.5	*Selenium	Se	79
<i>Chromium</i>	Cr	52	*SILICON	Si	28
<i>Cobalt</i>	Co	59	SILVER (Argentum)	Ag	108
COPPER (Cuprum)	Cu	63	SODIUM (Natrium)	Na	23
*FLUORINE	F	19	<i>Strontium</i>	Sr	88
<i>Gold</i> (Aurum)	Au	197	*SULPHUR	S	32
*HYDROGEN	H	1.008	TIN (Stannum)	Sn	119
*IODINE	I	127	<i>Tungsten</i> (Wolfram)	W	184
IRON (Ferrum)	Fe	56	ZINC	Zn	65
LEAD (Plumbum)	Pb	207			

## CHAPTER II

### CHEMICAL NOMENCLATURE

EVERYTHING unknown is more or less mysterious, and the mystery surrounding chemical transformations is increased, rather than lessened, by the constant use of terms which, to an outsider, suggest some occult jargon of the dark ages. And yet these terms are formed and used upon a system which is nothing if not simple, and, as a matter of fact, most of the confusion has arisen from the attempt to blend popular and scientific terms. The former, derived as a rule from some striking property of the substance, are often very misleading; the latter, based upon definite principles, are mathematically exact.

An element has already been defined as a substance which defies analysis, which has never yet been broken up into any simpler substances, and whose particles are therefore assumed to consist of but one kind of matter. To mark this unity of structure all elements have single names like oxygen, iron, carbon, chlorine. Some of the elements first discovered have popular names as well, based upon some striking property; thus sulphur is often called brimstone—the stone which burns—and mercury is called quicksilver, or living—*i.e.*, running—silver, a name which reappears in its chemical symbol, Hg, for *hydrargyrum*, the Greek word for liquid silver. Again, as will appear later on, graphite, plumbago, or black lead, are all names for a special form of carbon, as diamond is for the crystalline form, and soot, lampblack, and the various charcoals are for other forms of the same element.

When two elements combine, the new compound shows its origin in its name, distinguished by the termination *-ide*; thus sulphur and oxygen form sulphur oxide, sodium burned in chlorine gas forms sodium chloride, iodine sprinkled upon phosphorus forms phosphorus

iodide, and so on. We say sulphur oxide; why not oxygen sulphide? Just as in naming a person the Christian name is given first, followed by the family name, so in the naming of chemical compounds a certain order is observed, connected with the behaviour of the different elements under the action of an electric current. As described on pp. 54-55, when a current of electricity is passed through a chemical compound, preferably in solution, the substance is usually decomposed, one constituent appearing at the positive and the other at the negative electrode. In this way the elements have been arranged in order, from potassium and the other metals, which are all electro-positive elements, down to oxygen, which is generally regarded as the most electro-negative, though some maintain that the halogens (iodine, bromine, chlorine, and fluorine) should close the list. The following is the order generally accepted, and it is to be noted that any substance in the series is positive towards those on the right, but negative towards those on the left; that is to say, its electric standing is a purely relative matter:—

+	Potassium.	Sodium.	Calcium.	Magnesium.	Aluminium.	Zinc.	Iron.	Tin.	Lead.	Hydrogen.	Antimony.	Bismuth.	Copper.	Mercury.	Silver.	Platinum.	Gold.	Silicon.	Carbon.	Nitrogen.	Phosphorus.	Sulphur.	Iodine.	Bromine.	Chlorine.	Fluorine.	Oxygen.	—
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Generally speaking, then, in naming a compound of two elements, the metal or other electro-positive element comes first, and the electro-negative element last; phosphorus iodide, not iodine phosphide; calcium carbide, not carbon calcide.

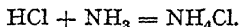
Very often the same elements may combine in several different proportions; thus carbon forms at least two oxides, and nitrogen no fewer than five. These are distinguished by the Greek prefixes mon- or mono- (1), di- (2), tri- (3), tetra- (4), penta- (5), hexa- (6), and so on; thus we have sulphur dioxide,  $\text{SO}_2$ , and sulphur trioxide,



$\text{SO}_3$ , while the oxides of nitrogen corresponding to the formulæ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_2$  (or  $\text{NO}$ ),  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$  (or  $\text{NO}_2$ ), and  $\text{N}_2\text{O}_5$ , are called nitrogen mon-, di-, tri-, tetr-, and pent-oxide respectively.

Before passing from binary compounds—those containing two elements—a word of caution is needed in regard to popular names. Many of these binary compounds have been known for centuries, and in consequence their popular names are too deeply rooted to be readily removed. When hydrogen burns in chlorine a new gas is formed which is, strictly speaking, hydrogen chloride,  $\text{HCl}$ , but which is still variously known as spirits of salt, muriatic acid, and hydrochloric acid, this last being the name in common use to-day, even among chemists. In the same way the fumes of burning sulphur, properly called sulphur dioxide,  $\text{SO}_2$ , are often called improperly sulphurous acid, just as carbon dioxide,  $\text{CO}_2$ , is widely known as carbonic acid. The table at the end of this chapter will be found useful in clearing up any difficulties arising from the use of popular names.

It was stated above that the termination *-ide* was employed for combinations of two elements. Very often, however, especially in organic chemistry, atoms of several elements are grouped together in a fairly permanent way, so closely and so persistently as to form a combination which behaves like an element. When hydrochloric acid and ammonia are allowed to mix, they form a solid substance, popularly known as sal-ammoniac, and chemically as ammonium chloride. The action of these two gases is represented by the following equation:—



Hydrogen Chloride and Ammonia form Ammonium Chloride.

This new substance contains three different elements, yet it is called ammonium chloride, as if the group  $\text{NH}_4$  were a single atom of an imaginary metal ammonium. From a comparison of the different compounds which may be obtained from this substance with the similar

potassium compounds, it is easily seen that the group  $\text{NH}_4$  does behave like a metal; is, in fact, a metallic *radical*. Thus from potassium (K) we have—

KCl,	Potassium	chloride.
KBr	„	bromide.
KI	„	iodide.
$\text{KNO}_3$	„	nitrate.
$\text{K}_2\text{SO}_4$	„	sulphate.
$\text{K}_2\text{CO}_3$	„	carbonate.

These are exactly comparable with the following ammonium ( $\text{NH}_4$ ) compounds:—

$\text{NH}_4\text{Cl}$ ,	Ammonium	chloride.
$\text{NH}_4\text{Br}$	„	bromide.
$\text{NH}_4\text{I}$	„	iodide.
$\text{NH}_4\text{NO}_3$	„	nitrate.
$(\text{NH}_4)_2\text{SO}_4$	„	sulphate.
$(\text{NH}_4)_2\text{CO}_3$	„	carbonate.

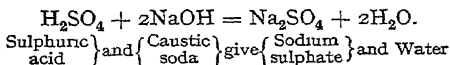
In fact the group  $\text{NH}_4$ , or ammonium, is sometimes written Am, as if ammonium were an actual metal, and in that case ammonium carbonate would appear as  $\text{Am}_2\text{CO}_3$ , exactly like potassium carbonate,  $\text{K}_2\text{CO}_3$ . Many such groups or radicals occur in organic chemistry; thus the group  $\text{C}_2\text{H}_5$  or ethyl yields ethyl iodide  $(\text{C}_2\text{H}_5)\text{I}$ , comparable with potassium iodide, KI; ethyl hydroxide or spirits of wine  $(\text{C}_2\text{H}_5)\text{OH}$ , like potassium hydroxide, KOH; ethyl oxide  $(\text{C}_2\text{H}_5)_2\text{O}$ , better known as ether, resembling in formula potassium oxide,  $\text{K}_2\text{O}$ , and so on all through. Besides metallic or basic radicals, groups of elements behaving like metals in combinations, there are also acid radicals, common to all the compounds formed by the same acid. Thus sulphuric acid has a formula  $\text{H}_2\text{SO}_4$ , in which the diad group  $\text{SO}_4$  combines with  $\text{H}_2$ , as it were. The following are the formulæ of some well-known sulphates:—

Potassium sulphate,	$\text{K}_2\text{SO}_4$ .	Copper sulphate,	$\text{CuSO}_4$ .
Sodium	„ $\text{Na}_2\text{SO}_4$ .	Iron (ferrous)	„ $\text{FeSO}_4$ .
Ammonium	„ $(\text{NH}_4)_2\text{SO}_4$ .	Zinc	„ $\text{ZnSO}_4$ .
Calcium	„ $\text{CaSO}_4$ .	Ferric	„ $\text{Fe}_2(\text{SO}_4)_3$ .
Magnesium	„ $\text{MgSO}_4$ .	Aluminium	„ $\text{Al}_2(\text{SO}_4)_3$ .

From these it appears that sulphates are characterised by the presence of the group  $\text{SO}_4$ ; in fact, sulphuric acid itself may be called hydrogen sulphate,  $\text{H}_2\text{SO}_4$ . In the same way nitrates are marked by the group  $\text{NO}_3$ , derived from nitric acid,  $\text{HNO}_3$ . Both basic and acid radicals are often enclosed in brackets, especially when the radical is multiplied, as in the formulæ given above for ammonium sulphate, and ferric or aluminium sulphates. Some of the very common basic radicals are even written in contraction symbols, like Am for ammonium ( $\text{NH}_4$ ), Et for ethyl ( $\text{C}_2\text{H}_5$ ), Me for methyl ( $\text{CH}_3$ ), Ph for phenol ( $\text{C}_6\text{H}_5$ ), T for the radical of tartaric acid ( $\text{C}_4\text{H}_4\text{O}_6$ ),  $\bar{\text{A}}$  for the radical of acetic acid ( $\text{C}_2\text{H}_3\text{O}_2$ ), and many others. In this way the formula of lead acetate (sugar of lead) could be written  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , or, more shortly,  $\text{Pb}_2\bar{\text{A}}$ , and that of potassium hydrotratarate (cream of tartar)  $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ , or simply  $\text{KHT}$ . With the exception of ammonium, such contractions rarely occur outside the field of organic chemistry, and even their number is limited.

The terms "acid" and "basic" have been used without explanation, and since they are of very common occurrence, it is time to define them. The common conception of an acid is a substance with a sour taste. It may be a solid like tartaric, citric, or oxalic acids; a liquid like oil of vitriol or aquafortis, the popular names for sulphuric and nitric acids; or a gas like hydrochloric acid. Since, however, many real acids have no special taste, and, on the other hand, many sour substances are not reckoned acids at all, some other distinction is necessary. Many of the strong acids are poisonous, and in any case it is never safe to taste an unknown substance, so the test is generally one which appeals to the eye. When purple cabbage is pickled in vinegar its colour changes to red, and any other dilute acid will affect purple cabbage in the same way. The vegetable usually taken now is blue litmus, sold in little blue lumps, and generally used either as an infusion of these or as litmus

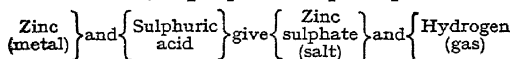
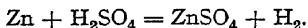
paper—white blotting paper dipped in this blue solution. All acids turn blue litmus red, or at least purple, but the blue colour may be restored by adding potash, soda, ammonia, or even lime-water. These substances which reverse the colour effects of acids are called *alkalis*. They have generally a soapy feel and taste, and, besides their action on red litmus, are able to turn turmeric, and certain other vegetable yellows, brown. If dilute sulphuric acid be reddened by a little litmus and a solution of caustic soda be added cautiously, stirring all the time, the red colour will be gradually discharged, and at last a point will be reached when the addition of one drop more of soda gives a decided blue, or that of one drop more of acid a decided red. At this stage the acid has been neutralised, and if now the purple solution be evaporated to dryness, the result is a substance which is neither acid nor alkaline, neither sulphuric acid nor soda, but a neutral *salt*, called sodium sulphate, or sulphate of soda. This action may be expressed in the form of a chemical equation :—



An alkali, then, is a substance capable of neutralising an acid and forming a salt, and it is generally recognised by its colour action upon red litmus, yellow turmeric, or other "indicator". The common alkalis are ammonia, potash, soda, lime, and magnesia.

When vinegar or any other acid is dropped upon baking-soda, or any other carbonate, effervescence takes place, owing to the liberation of carbonic-acid gas, and this reaction may be used as another handy test of an acid. All acids, therefore, in the popular sense are sour, turn blue litmus red, and decompose carbonates with effervescence. But the real definition of an acid arises from its chemical constitution. All acids in the chemical sense contain hydrogen, which is capable of being ex-

changed for a metal or a metallic radical; that is, a group of elements equivalent to a metal. Sulphuric acid has a formula  $\text{H}_2\text{SO}_4$ , but when sulphuric acid acts on zinc the result is that the hydrogen of the acid is expelled, and a new substance, zinc sulphate, is formed, having a formula  $\text{ZnSO}_4$ ,  $\text{H}_2$  having been exchanged for Zn. Zinc sulphate is an example of a *salt*, the term being used without any reference to taste to denote all similar substitution products of acids, in which all or part of their hydrogen has been replaced by a metal. In this change the metal zinc has acted as a *base* for the operations of the acid.



When sulphur is burned in oxygen the result is a gaseous oxide which, when dissolved in water, behaves like an acid, and a similar result is obtained by burning phosphorus or carbon; these give acid oxides. When a strip of magnesium is burned in air, however, magnesia ( $\text{MgO}$ ) is formed—a white solid which is distinctly alkaline. Lastly, when iron wire is burned in air, or when iron is allowed to rust, oxides of iron are formed, which are neither acid nor alkaline. These were called bases in the early days of chemistry, when acids were looked upon simply as oxides. Thus when carbonic-acid gas is bubbled through lime-water, the result is a white powder, calcium carbonate, or carbonate of lime,  $\text{CaCO}_3$ , formed by the carbonic acid gas ( $\text{CO}_2$ ) combining with the lime ( $\text{CaO}$ ) or calcium oxide. Hence arose the popular name, carbonate of lime, regarding lime as the base and carbonic acid gas as the acid, and indeed the formula of this substance used to be written  $\text{CaO} \cdot \text{CO}_2$ . But carbonic-acid gas is not an acid at all in the modern sense, since it contains no hydrogen; it is only an acid oxide which requires water to become a genuine acid,

and the real carbonic acid has a formula  $\text{H}_2\text{CO}_3$ , or  $\text{H}_2\text{O}\cdot\text{CO}_2$ , according to the old ideas. Chemists therefore no longer speak of carbonate of lime, but of calcium carbonate, treating the metal itself as base; but in common language the term "base" may be taken to include not only the metal, but also its oxides and hydroxides, so long as these never furnish acids by addition of water. Basic oxide is thus opposed to acid oxide, as electro-positive is opposed to electro-negative.

When the hydrogen of an acid is only partially replaced by a metal the result is an acid salt, or hydrogen salt, which may or may not have a sour taste. The formula of carbonic acid is  $\text{H}_2\text{CO}_3$ , in which either or both atoms of hydrogen may be replaced by the monad metal sodium (Na). If all the hydrogen be replaced, the result is a normal salt, sodium carbonate or soda-ash,  $\text{Na}_2\text{CO}_3$ ; but if only half the hydrogen is replaced, or—which comes to the same thing—more carbonic acid is added, the result is baking-soda, sodium bicarbonate or hydrocarbonate,  $\text{NaHCO}_3$ . When there is more base present than is required to displace all the hydrogen, a basic salt may be formed; thus white lead is basic lead carbonate, containing the base lead oxide in addition to the normal carbonate; verdigris is basic copper acetate, and so on.

Again, on looking at the formulæ of some typical acids, it is seen that some of them, like nitric acid,  $\text{HNO}_3$ , contain only one atom of hydrogen; others, like sulphuric acid,  $\text{H}_2\text{SO}_4$ , contain two atoms; others, like phosphoric acid,  $\text{H}_3\text{PO}_4$ , three atoms; others four atoms, like silicic acid,  $\text{H}_4\text{SiO}_4$ . These are distinguished as mono-, di-, tri-basic acids, etc., since the number of monad metallic bases which they can take depends upon the number of hydrogen atoms available. Thus nitric acid,  $\text{HNO}_3$ , can have only one nitrate of potassium,  $\text{KNO}_3$ , since there is only one hydrogen atom present, but sulphuric acid,  $\text{H}_2\text{SO}_4$ , may form the normal potassium sulphate,  $\text{K}_2\text{SO}_4$ , and also an acid sulphate or hydrogen sulphate,  $\text{KHSO}_4$ , very often called a bisulphate.

A tribasic acid like phosphoric,  $\text{H}_3\text{PO}_4$ , may have three different sodium salts; trisodium phosphate,  $\text{Na}_3\text{PO}_4$ ; disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ ; and sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4$ . Finally two or more bases may combine with one acid, forming double or triple salts. Dolomite or magnesian limestone is a double carbonate of calcium and magnesium. Rochelle salt is potassium sodium tartrate, common alum is aluminium potassium sulphate, common window-glass contains calcium sodium silicate, while a well-known derivative of phosphoric acid is known popularly as "triple phosphate", from the fact that it contains three bases, calcium, magnesium and ammonium.

It often happens that an element has several oxides capable of forming acids, thus giving rise to a series of oxy-acids with increasing proportions of oxygen. In the early days of chemistry, when but few compounds were known, different degrees of oxidation were marked by the use of the prefixes proto- and per-; thus two oxides of iron were known, corresponding to the formulæ  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ ; the former was called protoxide of iron or ferrous oxide, the latter peroxide of iron, or sometimes sesquioxide, from the prefix sesqui-, meaning one and a half, since that is the proportion of oxygen atoms to iron in this special case. Later on the terminations -ous and -ic were used, the former for the lower proportion of oxygen or other electro-negative element—*i.e.*, for the higher proportion of metal—and the latter for the higher proportion of oxygen. Thus  $\text{FeO}$  is the formula of ferrous oxide, the base of all the ferrous salts, like ferrous sulphate,  $\text{FeSO}_4$ , while  $\text{Fe}_2\text{O}_3$  represents ferric oxide, the base of the ferric salts, such as ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , in which the diad group,  $\text{SO}_4$ , has taken the place of an atom of oxygen. Sometimes, especially in pharmacy, we meet with the prefix sub-, to indicate a lower oxide or the like; thus calomel,  $\text{HgCl}$ , is called by druggists subchloride of mercury, and corrosive sublimate,  $\text{HgCl}_2$ , perchloride of mercury, instead of the modern names

mercurous and mercuric chloride, respectively. The prefix per-, strictly speaking, is applied to the highest known oxide or similar compound, as, for instance, in hydrogen peroxide,  $\text{H}_2\text{O}_2$ , which readily gives up its extra atom of oxygen and becomes water. Similarly, the black oxide of manganese, formerly so much in demand for making oxygen, has a formula  $\text{MnO}_2$ , and is properly called manganese dioxide; it was formerly called peroxide of manganese, but a higher oxide has meanwhile been discovered corresponding to the formula  $\text{MnO}_3$ , so that to avoid confusion the only safe names are those which give actual numbers, such as manganese trioxide, phosphorus pentachloride,  $\text{PCl}_5$ , triferric-tetroxide,  $\text{Fe}_3\text{O}_4$ , and the like.

Oxy-acids still retain the terminations -ous and -ic within certain limits. Sulphuric acid,  $\text{H}_2\text{SO}_4$ , forms a series of salts called *sulphates*, having the general composition  $\text{M}_2\text{SO}_4$ , but there is also *sulphurous* acid,  $\text{H}_2\text{SO}_3$ , containing 16 parts less oxygen, and this forms a series of salts called *sulphites*, of the general composition  $\text{M}_2\text{SO}_3$ . The removal of another oxygen atom gives  $\text{H}_2\text{S}_2\text{O}_4$ , which is *hyposulphurous* acid (Gr. *hypo*, under), and which forms *hyposulphites*; lower down it is impossible to go, since there is no such compound as  $\text{H}_2\text{SO}$ . The whole series is very well seen in the oxy-acids of chlorine, beginning with hydrochloric acid,  $\text{HCl}$ , which is really hydrogen chloride, and forms chlorides. Then comes  $\text{HClO}$ , hypochlorous acid, forming hypochlorites;  $\text{HClO}_2$ , chlorous acid, forming chlorites;  $\text{HClO}_3$ , chloric acid, forming chlorates; and, lastly,  $\text{HClO}_4$ , perchloric acid, forming perchlorates. In the same way we have hydrogen sulphide or sulphuretted hydrogen,  $\text{H}_2\text{S}$ , forming sulphides; there is no substance corresponding to  $\text{H}_2\text{SO}$ ; then comes hyposulphurous acid,  $\text{H}_2\text{S}_2\text{O}_4$ ; sulphurous acid,  $\text{H}_2\text{SO}_3$ ; sulphuric acid,  $\text{H}_2\text{SO}_4$ ; persulphuric acid,  $\text{H}_2\text{SO}_5$ ; and even perdisulphuric acid,  $\text{H}_2\text{O}_2 \cdot 2\text{SO}_3$ , or  $\text{H}_2\text{S}_2\text{O}_8$ . The substance commonly called hyposulphite of soda, the familiar "hypo" of photo-



graphers, has a formula  $\text{Na}_2\text{S}_2\text{O}_3$ , and is not sodium hyposulphite at all, but sodium thiosulphate, another instance of chemical discovery having outrun ill-founded nomenclature.

Many popular names are exceedingly misleading in this respect; thus salts of sorrel are really not salts at all, but an acid—oxalic acid; pyrogallic acid, again, the “pyro” of photographers, is not an acid at all in the chemical sense, but rather akin to an alcohol, being a hydroxybenzene or phenol; spirit of salt is not an alcohol, as its name would seem to imply, but simply an old-fashioned name for hydrochloric acid.

Water presents a difficulty of nomenclature. Many substances combine with water to form crystalline forms, and this “water of crystallisation” is easily expelled by heat, when the substance resumes its original form. Ordinary copper sulphate or blue vitriol exists in blue crystals, but these on being heated to above  $100^\circ \text{C}$ . part with five molecules of water, leaving pure copper sulphate as a white powder which, however, turns blue immediately on being moistened. White copper sulphate has a formula  $\text{CuSO}_4$ , but the crystals have a formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; this represents the *hydrate*, or hydrated copper sulphate. In the same way sodium carbonate or soda-ash is  $\text{Na}_2\text{CO}_3$ , but the hydrated carbonate takes the familiar form of soda crystals, or washing-soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . The subject of water of crystallisation will receive further treatment in the chapter on water.

Strange to say, water may behave as an acid in the chemical sense; that is to say, it contains atoms of hydrogen which may be wholly or partly replaced by a metal if that metal is “strong” enough. If metallic sodium be dropped into water, half of the hydrogen in the water is liberated, and the metal combines with the other half and the oxygen to form caustic soda,  $\text{NaOH}$ . Substances of this type used to be called hydrates, but the name hydrate is now restricted to substances containing water of crystallisation, and these water salts, or

substitution products of water, are called *hydroxides*. Caustic soda,  $\text{NaOH}$ , is therefore sodium hydroxide; and slaked lime,  $\text{Ca}(\text{OH})_2$ , calcium hydroxide. The distinction is a useful one, since in hydrates the water of crystallisation is loosely held, and can, as a rule, be expelled on heating the substance slightly above the boiling-point of water, whereas in hydroxides there is genuine chemical combination, often of a very close nature, demanding considerable pains in order to expel the water again.

As an example of the seeming confusion due to the employment of different systems of nomenclature, take the substance represented by the formula  $\text{NaHCO}_3$ . This is variously called—

Baking soda.	Sodium bicarbonate.
Bicarbonate of soda.	Sodium hydrocarbonate.
Acid carbonate of soda.	Sodium hydrogen carbonate.
Sodic hydic carbonate.	

The following list of chemicals which have popular names will perhaps be of some service :—

POPULAR NAMES OF COMMON CHEMICALS

Popular Name.	Chemical Name.	Formula.
Alabaster	Calcium sulphate	$\text{CaSO}_4$
Alum	Potassium aluminium sulphate	$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
Antichlor	Sodium thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Antifebrin	Acetanilide	$\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{COCH}_3$
Aqua fortis	Nitric acid	$\text{HNO}_3$
Aqua regia	Nitro - hydrochloric acid	$\text{HNO}_3 + \text{HCl}$
Argol, Cream of Tartar	Potassium hydro-tartrate	$\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ or KHT
Aspirin	Acetyl salicylic acid	$\text{C}_9\text{H}_8(\text{COOH})\text{O} \cdot \text{COCH}_3$
Baking soda	Sodium bicarbonate	$\text{NaHCO}_3$
Barytes, or heavy spar	Barium sulphate	$\text{BaSO}_4$
Bauxite	Hydrated alumina	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Black ash	Sodium carbonate + calcium sulphide	$\text{Na}_2\text{CO}_3 + \text{CaS}$
Black Lead, Plumbago, or Graphite	Carbon	C

POPULAR NAMES OF COMMON CHEMICALS (*continued*)

Popular Name.	Chemical Name.	Formula
Bleaching powder, or "Chloride of Lime"	Calcium hypo- chlorite + calcium chloride	$\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$
Blende	Zinc sulphide	$\text{ZnS}$
Bluestone, or Blue vitriol	Copper sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Bone ash	Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$
Boric acid	Boric acid	$\text{H}_3\text{BO}_3$
Borax	Sodium diborate	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Brimstone	Sulphur	$\text{S}$
British gum	Dextrin	$\text{C}_6\text{H}_{10}\text{O}_5$
Butter of antimony	Antimony ter- chloride	$\text{SbCl}_3$
Calamine	Zinc carbonate	$\text{ZnCO}_3$
Calomel	Mercurous chloride	$\text{Hg}_2\text{Cl}_2$
Cane sugar	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Carbolic acid	Phenol	$\text{C}_6\text{H}_5(\text{OH})$
Carborundum	Silicon carbide	$\text{SiC}$
Chalk, Marble, Lime- stone, Calcite, Ice- land spar	Calcium carbonate	$\text{CaCO}_3$
Chili saltpetre	Sodium nitrate	$\text{NaNO}_3$
China clay, Kaolin, Fuller's earth	Aluminium silicate	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Chinese white	Zinc oxide	$\text{ZnO}$
Chloramine-T	Sodium <i>p</i> -toluene sulphochloramide	$\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NClNa}$
Chrome alum	Chromium alumin- ium sulphate	$\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
Chrome ironstone	Ferrous chromite	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$
Chrome yellow	Lead chromate	$\text{PbCrO}_4$
Cinnabar	Mercuric sulphide	$\text{HgS}$
Copperas, or green vitriol	Ferrous sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Copper pyrites	Copper-iron sulphide	$\text{CuFeS}_2$
Corrosive sublimate	Mercuric chloride	$\text{HgCl}_2$
Cream of tartar	Potassium hydro- tartrate	$\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ or KHT
Dolomite	Calcium-magnesium carbonate	$\text{CaCO}_3 \cdot \text{MgCO}_3$
Eau de Javelle	Potassium hypo- chlorite + chloride	$\text{KClO} + \text{KCl}$
Eau de Labarraque	Sodium hypo- chlorite + chloride	$\text{NaClO} + \text{NaCl}$
Emerald green	Copper arsenite	$\text{Cu}_3\text{HAsO}_4$
Emery, or Corun- dum	Aluminium oxide	$\text{Al}_2\text{O}_3$
Epsom salts	Magnesium sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Essence of Mirbane	Nitrobenzene	$\text{C}_6\text{H}_5(\text{NO}_2)$
Euchlorine	Chlorine + chlorine di-oxide	$\text{Cl}_2 + \text{ClO}_2$

POPULAR NAMES OF COMMON CHEMICALS (*continued*)

Popular Name.	Chemical Name.	Formula.
Fire damp or marsh gas	Methane	$\text{CH}_4$
Fluorspar, fluorite	Calcium fluoride	$\text{CaF}_2$
Formalin	Formaldehyde	$\text{H}\cdot\text{CHO}$
French chalk, Talc, or Soapstone	Magnesium silicate	$6\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$
Fruit sugar	Levulose or Fructose	$\text{C}_6\text{H}_{12}\text{O}_6$
Fusel oil	Amyl alcohol	$\text{C}_5\text{H}_{11}\text{OH}$
Galena	Lead sulphide	$\text{PbS}$
Glauber salt	Sodium sulphate	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$
Grape sugar, or Glucose	Dextrose	$\text{C}_6\text{H}_{12}\text{O}_6$
Gypsum	Calcium sulphate	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
Hæmatite, red	Ferric oxide	$\text{Fe}_2\text{O}_3$
Hæmatite, brown or yellow	Ferric hydroxide	$2\text{Fe}_2\text{O}_3\cdot 3\text{H}_2\text{O}$
Heavy spar	Barium sulphate	$\text{BaSO}_4$
Horn silver	Silver chloride	$\text{AgCl}$
Hydroquinone	Dihydroxybenzene	$\text{C}_6\text{H}_4(\text{OH})_2$
"Hyposulphite" of soda	Sodium thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$
Invert sugar	Dextrose + levulose	$\text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$
Ivory black	Carbon	$\text{C}$
Lampblack	Carbon	$\text{C}$
Laughing gas	Nitrous oxide	$\text{N}_2\text{O}$
Litharge or Massicot	Lead oxide	$\text{PbO}$
Liver of sulphur	Potassium sulphide	$(\text{K}_2\text{S})_n$
Lunar caustic	Silver nitrate	$\text{AgNO}_3$
Malachite	Basic copper carbonate	$\text{CuCO}_3\cdot \text{Cu}(\text{OH})_2$
Malt sugar	Maltose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Meerschaum	Magnesium silicate	$2\text{MgO}\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$
Microcosmic salt	Sodium-ammonium hydrogen phosphate	$\text{Na}(\text{NH}_4)\text{HPO}_4$
Milk sugar	Lactose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Nordhausen acid	Sulphuric acid + sulphur trioxide	$\text{H}_2\text{S}_2\text{O}_7$
Oil of vitriol, or vitriol	Sulphuric acid	$\text{H}_2\text{SO}_4$
Oleum	Fuming sulphuric acid	$\text{H}_2\text{S}_2\text{O}_7$
Orpiment	Arsenic trisulphide	$\text{As}_2\text{S}_3$
Pearl ash	Potassium carbonate	$\text{K}_2\text{CO}_3$
Pearl white	Bismuth nitrate	$\text{Bi}(\text{NO}_3)_3$
Phosgene	Carbonyl chloride	$\text{COCl}_2$
Picric acid	Trinitrophenol	$\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot \text{OH}$
Pink vitriol	Manganous sulphate	$\text{MnSO}_4\cdot 5\text{H}_2\text{O}$
Plaster of Paris	Calcium sulphate	$\text{CaSO}_4\cdot \frac{1}{2}\text{H}_2\text{O}$
Potashes, pearl-ash	Potassium carbonate	$\text{K}_2\text{CO}_3$

POPULAR NAMES OF COMMON CHEMICALS (*continued*)

Popular Name.	Chemical Name.	Formula.
Prussian blue	Ferric ferrocyanide	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
Prussiate of potash, yellow	Potassium ferro-cyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$
Prussiate of potash, red	Potassium ferri-cyanide	$\text{K}_3\text{Fe}(\text{CN})_6$
Prussic acid	Hydrocyanic acid	$\text{H}(\text{CN})$ or $\text{HCy}$
Pyrites	Iron disulphide	$\text{FeS}_2$
"Pyrogallic acid"	Pyrogallol, trihydroxybenzene	$\text{C}_6\text{H}_3(\text{OH})_3$
Pyroligneous acid	Crude acetic acid	$\text{CH}_3\text{COOH}$ or $\text{HAc}$
Quartz or Rock crystal	Silicon oxide or silica	$\text{SiO}_2$
Quicklime	Calcium oxide	$\text{CaO}$
Quicksilver	Mercury	$\text{Hg}$
Realgar	Arsenic disulphide	$\text{As}_2\text{S}_3$
Rochelle salt	Potassium sodium tartrate	$\text{KNa}(\text{C}_4\text{H}_4\text{O}_6)$ or $\text{KNaT}$
Red lead	Lead oxide	$2\text{PbO} \cdot \text{PbO}_2$
Rouge, Colcothar, or Indian red	Ferric oxide	$\text{Fe}_2\text{O}_3$
Saccharin	Benzoic sulphimide	$\text{C}_6\text{H}_4\text{SO}_2 \cdot \text{NHCO}$
Sal-ammoniac	Ammonium chloride	$\text{NH}_4\text{Cl}$
Salt	Sodium chloride	$\text{NaCl}$
Saltcake	Sodium sulphate	$\text{Na}_2\text{SO}_4$
Saltpetre or nitre	Potassium nitrate	$\text{KNO}_3$
Salts of lemon	Potassium binoxalate	$\text{KH}(\text{C}_2\text{O}_4)$ or $\text{KH}\overline{\text{Ox}}$
Salts of sorrel	Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$ or $\text{H}_2\overline{\text{Ox}}$
Salts of tartar	Potassium carbonate	$\text{K}_2\text{CO}_3$
Scheele's green	Copper arsenite	$\text{CuHAsO}_3$
Sedative salts	Boric acid	$\text{H}_3\text{BO}_3$
Slaked lime	Calcium hydroxide	$\text{Ca}(\text{OH})_2$
Smelling salts	Ammonium sesquicarbonate	$(\text{NH}_4)_2\text{C}_3\text{O}_6$
Soda ash	Sodium carbonate	$\text{Na}_2\text{CO}_3$
Spirits of salts	Hydrochloric acid	$\text{HCl}$
Spirits of wine	Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$
Starch sugar	Glucose	$\text{C}_6\text{H}_{12}\text{O}_6$
Stassfurt salts	Potassium chloride	$\text{KCl}$
Sugar of lead	Lead acetate	$\text{Pb}(\text{CH}_3\text{COO})_2$ or $\text{Pb}_2\overline{\text{A}}$
"Superphosphate"	Calcium phosphate and sulphate	$\text{Ca}_3(\text{PO}_4)_2 + \text{CaSO}_4$
Sylvine	Potassium chloride	$\text{KCl}$
Tartar (in wine)	Potassium hydro-tartrate	$\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ or $\text{KHT}$
Tartar (on teeth)	Calcium carbonate	$\text{CaCO}_3$
Tartar emetic	Antimony oxy-tartrate	$\text{SbOK}(\text{C}_4\text{H}_4\text{O}_6)$ or $\text{SbOKT}$
Turnbull's blue	Ferrous ferricyanide	$\text{Fe}_2[\text{Fe}(\text{CN})_6]$
Verdigris	Basic copper acetate	$\text{Cu}(\text{CH}_3\text{COO})_2 + \text{Cu}(\text{OH})_2 + \text{H}_2\text{O}$

POPULAR NAMES OF COMMON CHEMICALS (*continued*)

Popular Name.	Chemical Name.	Formula.
Vermilion, Cinnabar	Mercury sulphide	$\text{HgS}$
Vinegar	Acetic acid	$\text{CH}_3\text{COOH}$ or $\text{H}\bar{\text{A}}$
Wall saltpetre	Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$
Washing soda, or Soda crystals	Sodium carbonate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Water gas	Hydrogen + carbon monoxide	$\text{H}_2 + \text{CO}$
Water glass	Sodium silicate	$\text{Na}_2\text{SiO}_3$
White lead	Basic lead carbonate	$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$
White precipitate	Mercury-ammonium chloride	$\text{HgCl NH}_2$
White vitriol	Zinc sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Witherite	Barium carbonate	$\text{BaCO}_3$
Wood spirit or Wood naphtha	Methyl alcohol	$\text{CH}_3\text{OH}$
Zinc white	Zinc oxide	$\text{ZnO}$

## CHAPTER III

### CHARACTERS OF CHEMICAL ACTION

AMONG the many unsolved problems presented by the physical universe few have so persistently thrust themselves into human affairs, have so long engaged the attention alike of the deepest thinkers and of "the man in the street", as those phenomena classed under the general name of Attraction. Whether it take the form of Cohesion—that attraction of particle to particle in the same substance which maintains solids in their form—or the wider form of Gravitation—attraction of masses irrespective of distance, which guides alike the fall of an apple and the movements of the solar and stellar systems—or that attraction of opposites which forms the outstanding feature of Electricity and Magnetism on one side, and of Chemistry on the other; in each and every case the *cause* of the phenomena is absolutely unknown. Many ingenious theories have been advanced to explain the fall of Newton's apple, while in chemistry the modern atomic theory is but a modified return to the ancient doctrine of Lucretius. Subsequent chapters of the present work may aim at giving a popular bird's-eye view of the manner in which chemical affinity acts, they may even succeed in laying down the lines along which it acts, but they make no pretence of explaining *how*, and much less *why*, such action takes place in the way it does, or takes place at all.

Everyday life presents numerous examples of chemical attraction or chemical affinity. When a piece of bread is toasted the white starch of the bread is converted into a yellowish-brown substance called dextrin, and this passes gradually into darker forms, ending with charcoal. A Seidlitz powder presents a similar phenomenon. In this case two white crystalline powders, one, baking soda, with an alkaline taste, the other strongly acid,

combine to form carbonic-acid gas, which escapes with effervescence and another substance, tartrate of soda, which remains in solution. Such a change illustrates two features of chemical action. As long as the powders are simply mixed in the dry state no change occurs; apparently the particles are not sufficiently close to act on each other. If, however, the powders are dissolved in water, the particles become infinitely small, invisible even under a microscope, and so have a better opportunity of coming into close quarters, producing, as already mentioned, a third substance, which differs entirely from the original powders, being a colourless gas. Unlike gravitation, then, chemical attraction acts only upon particles which are in absolute contact, or nearly so; unlike cohesion, chemical attraction is strongest between particles of different substances. Further, chemical attraction is distinguished by the production of new substances, often differing very widely in all their properties from the substances which produced them. Thus quicklime is a dry white powder, and sal-ammoniac is a white crystalline powder, both odourless, but on being intimately mixed and gently warmed, these substances produce the very pungent gas known as spirits of hartshorn, or ammonia. If a glass bottle full of ammonia gas be mixed with a similar bottle full of hydrochloric acid gas, these colourless gases immediately unite to form sal-ammoniac, a white crystalline solid, odourless, and neither acid nor alkaline in taste. If strong sulphuric acid is added to some sugar in a saucer, the sugar is at once attacked, swelling up into a mass of charcoal from which escape jets of steam, accompanied by the odour of caramel or burnt sugar. Gunpowder is a familiar example of a chemical change in which the three solids—charcoal, sulphur, and saltpetre—combine instantaneously to form various gases, with a different solid residue which forms a smoke. Smokeless powder is so called because the new products formed on explosion are entirely gaseous. Colour changes are common

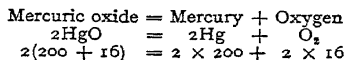


accompaniments of chemical action. Make up in different glasses solutions of the following substances: Sugar of lead, corrosive sublimate, tartar emetic, arsenic, manganese sulphate or pink vitriol, and zinc sulphate or white vitriol, then add to each a few drops of sulphuretted hydrogen in solution. Though all the liquids are colourless, solid coloured sulphides are formed: brownish-black sulphide of lead; sulphide of mercury, white, yellow, orange, and black; orange sulphide of antimony; yellow sulphide of arsenic; flesh-coloured sulphide of manganese; and white sulphide of zinc. Such changes form the basis of chemical analysis, since not only is the lead, for instance, removed in the form of solid sulphide, but the colour of the sulphide is often quite sufficient by itself to give a clue to the nature of the original substance. Similar colour changes form the stock-in-trade of the conjuror, who seems to produce different liquors at pleasure by pouring what looks like water into a series of vessels also containing some equally clear solution.

Some simple cases of chemical action may be taken as types. Very often this action is one of simple composition—two substances combining to form a third which contains all the materials of the other two. This is the case when ammonia is mixed with hydrochloric acid gas; the new substance, sal-ammoniac, contains all the elements of the original substances. If hydrogen and oxygen—both colourless gases—are mixed in the proportion of two to one by volume, the mixture is still a colourless gas, but let a light be applied, and violent chemical action occurs—an explosion, in fact, resulting in the formation of water, which contains all the hydrogen and oxygen, but no longer as simple gases.

Very often chemical action has an opposite result—that of decomposing a substance into its constituents. Red oxide of mercury is a heavy red powder apparently simple in structure, but when a little of this substance is heated in a dry test-tube it first turns black, then finally

disappears altogether from the place where it is heated, leaving a "mirror" of mercury at the cool end of the tube and giving off oxygen gas, which escapes. The change in this case may be represented by an equation:—



The middle line represents a chemical equation, in which O and Hg are the respective symbols for oxygen and

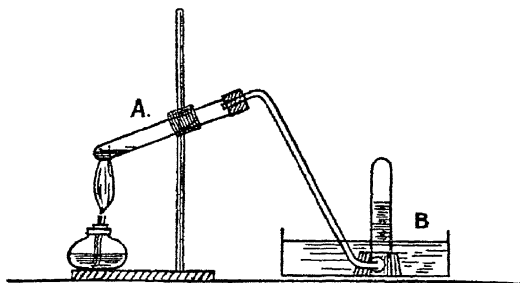


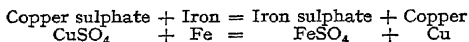
FIG. 3.—DECOMPOSITION OF MERCURIC OXIDE.

A, test-tube with oxide; B, pneumatic trough for collecting gas.

mercury (hydrargyrum); but besides being mere short-hand symbols, these carry a quantitative value as well; as shown in the lower line, O always means 16 parts by weight—say grammes—of oxygen, and Hg 200 parts of mercury, so that the chemical equation is really a short way of writing the following quantitative statement: 216 parts of mercuric oxide yield 200 parts of mercury and 16 parts of oxygen. This illustrates the most important feature of chemical change—namely, that whatever alteration there may be of the physical properties of the substances involved—taste, colour, smell, etc.—there is *no loss of weight* in the total quantity of substances taking part. Despite any of the alterations

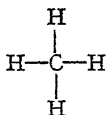
in physical form, none of the matter is destroyed nor is any created.

A great many chemical changes fall under the head of displacement, one metal taking the place of another, one acid expelling another, and so on. If a knife-blade be dipped into a solution of bluestone or copper sulphate, the blade will become coated with copper, and if left long enough it will part with its own iron to the liquid and end by becoming a copper blade altogether, while the liquid will gradually alter in colour from blue to pale green. This displacement of copper by iron may be written thus :—

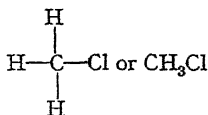


Some very pretty experiments may be made to illustrate displacement or single decomposition. Hang a piece of granulated zinc in copper sulphate solution. In a few hours the liquid will be found colourless, while the zinc will become coated with reddish-brown masses of copper. Hang a similar piece of zinc in a solution of lead acetate or sugar of lead; beautiful fern-like crystals of lead form round the zinc, constituting what is sometimes called "the tree of Saturn", and the liquid is now acetate of zinc instead of the original acetate of lead. In the same way a strip of copper foil displaces mercury from a solution of corrosive sublimate. Displacement of one acid by another is of common occurrence in chemistry, and forms the basis of several manufacturing processes. Thus in "health-salts" tartaric acid expels carbonic acid from baking-soda, forming bitartrate of soda, instead of bicarbonate of soda. If sulphuric acid be added to common salt or sodium chloride, white pungent acid fumes come off, showing that the hydrochloric acid of the salt is being expelled by sulphuric acid, thus forming "salt-cake" or sodium sulphate, instead of the chloride. This substitution or displacement may be carried to a great length with the carbon compounds, chlorine gas being used to replace hydrogen. For instance, methane,

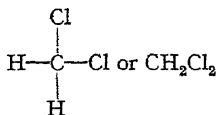
better known as marsh-gas or fire-damp, has a chemical formula  $\text{CH}_4$ , or pictorially—



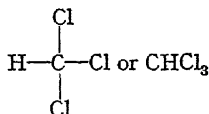
By treatment with chlorine a series of substitution products may be obtained in which more or less hydrogen has been replaced by chlorine, giving successively methyl chloride—



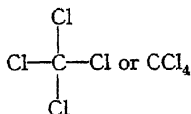
ethylene dichloride—



chloroform—

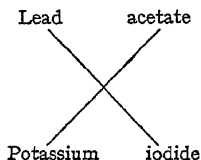


and finally carbon tetrachloride (used in dry-cleaning and fire extinguishers), in which none of the original hydrogen is left—



At each stage the hydrogen is removed, in combination with some more of the chlorine, in the form of hydrochloric acid gas.

In a great many cases double decomposition occurs—both substances being affected. Into a solution of lead acetate pour a little potassium iodide solution; the result is to give a yellow deposit which turns out to be lead iodide, while potassium acetate remains in solution. Here the action may be represented as follows, the cross lines giving the result of the combination :—



Numerous examples of this kind of action will occur later on.

By way of summary it may be stated that chemical action occurs most readily when the particles are in absolute contact, as in gases or solutions or the molten state; it acts most strongly between dissimilar substances; as a result of this action at least one new substance is formed, termed a chemical "compound", as opposed to a mere mixture; compounds often differ completely from their constituents in physical features, colour, taste, smell, and the like; lastly, in all chemical changes there is no loss of weight.

## CHAPTER IV

### WATER

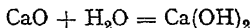
SINCE chemical action is strongest when the combining substances are in a state of minute division, such division is often attained by powdering the substances as finely as possible and then mixing them thoroughly. In many cases this is not sufficient to induce chemical action; thus gunpowder is an intimate mixture of charcoal, sulphur, and saltpetre, but these ingredients lie side by side without combining till the mixture is fired. Baking-soda and tartaric acid may be ground up together without any chemical action, but on adding a little water, effervescence follows at once. Sometimes the equilibrium of the mixture is disturbed mechanically, as when dynamite is exploded by a sudden blow, or a charge of electricity may be used as the exciting instrument; but generally the application of heat or the formation of a solution is quite sufficient to induce new combinations when such are possible.

When crystals of saltpetre are dropped into water they turn smaller and finally disappear, being invisible even under the microscope. Judging from its behaviour, a solution is more than a mere arrangement of liquid and solid particles in juxtaposition—changes of temperature and volume often accompany solution, and the substance dissolved is much more active than in the free state. When more saltpetre is added to water it also dissolves, until in this way a cold saturated solution may be obtained, when the water is unable to dissolve any more of the solid. On heating the liquid, however, its solvent powers are greatly increased, and boiling water may dissolve ten times as much substance as cold water. Salt is a curious exception to this rule, since its solubility in hot or cold water is practically the same. Since a hot solution usually contains more solid substance than a cold

one, it follows that when a hot solution cools, some of the solid must come out of solution, and this may happen in either of two ways. When a hot solution of saltpetre is allowed to cool, solid saltpetre separates in the form of crystals, and, by cooling slowly, these crystals may be obtained of considerable size and beauty. On the other hand, a hot solution of glue or starch forms a jelly or paste on cooling, thus giving a division of solids into crystalloids and colloids. Many substances are capable of existing in both conditions; thus sugar occurs commonly in crystals, but may also assume the non-crystalline condition of "barley-sugar". In many cases the solids thus separated from solution are found to have taken up some water, known as "water of crystallisation", since the presence of this water is often associated with a definite crystalline form. Thus pure dry (anhydrous) copper sulphate is a white powder, but on being dissolved in water it gives a blue solution, which on evaporating yields the well-known blue crystals of "bluestone", consisting of copper sulphate combined with five parts of water of crystallisation. In the same way soda-ash combines with water, forming the well-known soda-crystals, but in this case the water of crystallisation is loosely held, and such crystals, especially if kept in a warm place, speedily lose their definite form and crumble down into a shapeless powder. This readiness to part with water is known as "efflorescence", and is in marked contrast with the behaviour of other substances which are "deliquescent", *i.e.*, readily take up water, even from the air. Everybody knows that cooking-salt, if left in a damp place, speedily cakes into a solid mass; white copper sulphate exposed to damp becomes blue from water of crystallisation; lumps of calcium chloride left in a watch-glass will soon dissolve in water of their own collecting; and an open bottle of strong sulphuric acid left nearly full will fill and run over, having absorbed extra water from the air. Substances like these are very useful for drying gases, and for this purpose calcium

chloride or strong sulphuric acid are generally used—the latter being poured on bits of pumice, or other porous material, so as to increase the drying surface.

When water is poured on quicklime, a more intimate union takes place, considerable heat is evolved, the lime combines with the water and forms a genuine chemical compound—hydroxide of lime or slaked lime, differing in many respects from quicklime, and parting with its water only with considerable difficulty. An equation which shows this reaction is :—



Quicklime and Water give  $\begin{cases} \text{Slaked Lime} \\ \text{Calcium Hydroxide} \end{cases}$

The term “hydroxide” is now restricted to such combinations—the possession of water of crystallisation being covered by the word “hydrate”.

When a small piece of the metal sodium is dropped into a little water in a tea-cup, chemical action at once occurs between the liquid and the metal. The sodium melts into a ball, which swims violently on the surface, lessening as it goes, and finally disappears with a slight pop. The water now has a soapy feel, an alkaline taste, and turns red litmus paper blue; it is, in fact, no longer water, but sodium hydroxide or caustic soda in solution—the metal sodium having displaced some hydrogen gas from the water, uniting with the oxygen and the remaining hydrogen. This gives one method of analysing water into its two component elements—hydrogen and oxygen. Potassium behaves like sodium, but with more energy, liberating half of the hydrogen, which burns, and forming an hydroxide known as caustic potash. Other metals, however, are able to expel the whole of the hydrogen in water, forming an oxide with the oxygen. If steam be passed over heated zinc, hydrogen gas is liberated and zinc oxide is left. Scrap iron may be used instead of zinc, and hydrogen obtained in this way, though



containing impurities derived from the iron, was at one time used for lantern purposes as well as for ballooning.

When an electric current passes through water to which a few drops of sulphuric acid have been added to render it a better conductor, bubbles of gas appear—both where the current enters and leaves the liquid—and if the gases thus evolved are collected and examined, it is found that oxygen is formed where the current enters, and hydrogen at the other electrode. Thus by electrolysis—analysis by means of electricity—water may be

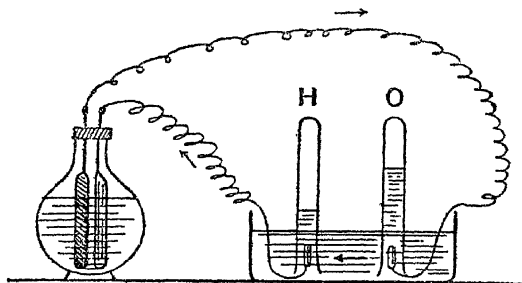


FIG. 4.—ELECTROLYSIS OF WATER.

resolved into two elementary gases : oxygen and hydrogen. Conversely, if the gases so obtained be mixed and exploded, water is formed. Water is, in fact, oxide of hydrogen; it is formed when hydrogen or anything containing hydrogen burns in air and, conversely, whenever any substance forms water on burning in air, that substance must have contained hydrogen. In this way the presence of hydrogen may be demonstrated in wood, coal, and most fuels; in oil, fat, and almost all food-stuffs, as well as in all common illuminants. Further, if the quantity of water so formed is collected and weighed, the amount of hydrogen can be calculated. This is a fact of importance in chemical analysis.

The appearance of hydrogen and oxygen at different electrodes in electrolysis suggests an electric division of the elements into positive and negative, the latter including those which, like oxygen, appear at the electrode (anode) connected with the positive pole of the battery. Generally speaking, hydrogen and all the metals appear where the current leaves the substance—*i.e.*, at the electrode (cathode) connected with the zinc or negative pole of the battery—and they will therefore be electro-positive, oxygen and similar substances being electro-negative. As mentioned on p. 29, the electro-chemical properties of the elements are made use of when naming their compounds; the electro-positive element, metal or hydrogen, is written first, then the electro-negative elements; thus  $\text{CuSO}_4$ , copper sulphate (cuprum);  $\text{KNO}_3$ , potassium nitrate (kali);  $\text{CaCO}_3$ , calcium carbonate, and so on, though popular phraseology often reverses the order, beginning with the acid and finishing with the base, sulphate of copper, carbonate of lime.

Since water is a very good solvent, it might be expected that pure water never occurs in nature. Even rain-water contains gases dissolved from the air, besides solid impurities in the form of soot and dust, and when absolutely pure water is wanted, recourse must be had to distillation. Surface water necessarily contains a fair amount of dissolved materials, solid, liquid, and gaseous, and spring water is often so highly charged with dissolved matters as to acquire a special colour, taste, or odour, becoming a "mineral water". Many mineral waters contain dissolved gases, especially carbonic-acid gas and sulphuretted hydrogen; others contain iron, and are known as chalybeate waters; silica is often held in solution in hot water and deposited as sinter on cooling, as in the famous pink-and-white terraces of New Zealand, now destroyed. But the most common substance found in water to any great extent is carbonate of lime, derived from limestone, chalk, or other calcareous rocks, and

held in solution by carbonic-acid gas. When such a water is boiled, the carbonic-acid gas is expelled, and the carbonate of lime held in solution is deposited as a "fur" upon the containing vessel. Slow evaporation produces the same result and gives rise to the formation of stalagmites and stalactites so common in limestone districts; the latter may be seen on a small scale on the under-side of almost any stone bridge. Water containing much lime does not readily form a lather with soap, since the latter is decomposed by lime and similar substances, and the water is then said to be "hard". When hardness is due to sulphates or any other substances not easily removable—generally sulphate of lime—it is said to be "permanent"; when, however, the hardness is due to carbonate of lime it is "temporary", because, as seen above, the carbonic acid may be expelled by boiling, and the lime removed as "fur". Temporary hardness may also be removed by Clark's method of adding more lime, and this explains the chemical action of many filters which soften as well as clarify the water passing through them. In hard water districts it is now common to find water-softeners in use to soften the water for home requirements. The hard water is passed through a cylindrical container charged with a powdered artificial zeolite, commercially known as "Permutite", which is made by fusing together a mixture of sand, china-clay and soda-ash. Similar zeolites of natural occurrence are found in the Greensands of America and Australia. Both the natural and the artificial products are complex silicates of alkali metals, iron and aluminium. The calcium and magnesium salts in the water react with the zeolite to form insoluble calcium and magnesium zeolite, and also a soluble sodium salt. The exhausted zeolite is revived by passing a concentrated solution of sodium chloride through it; this converts the calcium and magnesium zeolite back again into sodium zeolite ready for further use.

The activity of the zeolite may be reduced owing to the action of traces of other salts in the water, for example, iron. The effect is cumulative and, apparently, irreversible. Humic acid, which is derived from peat and is found in moorland and river water, is also injurious, particularly if it is associated with iron, as it often is.

In water analysis hardness is expressed in terms of carbonate of lime per gallon of 70,000 grains; thus 17 degrees hardness is equivalent to 17 grains of carbonate of lime per gallon. Continental analysts generally state the proportion per 100,000, instead of per gallon.

By way of comparison, the following table shows the average composition of a number of unpolluted natural waters. Permanent and temporary hardness figures are given as well as total solids, chlorine, carbon and nitrogen, all expressed as parts per 100,000.

Class of Water.	Total Solids.	Com- bined Nitrogen.	Organic Carbon.	Chlorine.	Hardness.	
					Tempor- ary.	Perma- nent.
Rain . . .	2.95	0.042	0.070	0.822	0.4	0.5
Upland Surface . . .	9.67	0.042	0.322	1.130	1.5	4.3
Deep Well . . .	43.78	0.522	0.061	5.11	15.8	9.2
Spring . . .	28.20	0.396	0.056	2.49	11.0	7.5

The quantities of carbon and nitrogen present are some indication of the amount of organic matter present in the total solids found; the chlorine is also an estimate of the inorganic dissolved salts as a whole.

Generally speaking, a drinking-water should be perfectly clear, without taste or odour, cool, aerated, and moderately soft. The presence of chlorides, ammonia, nitrates, and nitrites, renders a water suspicious, since these have most probably been acquired by sewage contamination. The chemical analysis of a drinking-water is, however, of very little use unless supported by

bacteriological examination, since it is the living germs of disease which have to be excluded if possible, and not simply their products. For the same reason some filters in the market are worthless or worse than worthless, since, while clarifying and otherwise improving the water, they are unable to arrest living germs of disease. The only filters able to sterilise a water by mechanical means are those constructed of finely-porous porcelain, such as the Pasteur-Chamberland and the Berkefeld filters. When proper appliances are not available, an infected water can readily be sterilised by boiling, preferably at intervals—the mouth of the vessel being closed by a plug of cotton wool to act as an air filter and exclude fresh germs. Chlorination, using either fresh bleaching powder or a hypochlorite disinfectant ("Milton", etc.), is just as effective as boiling and may be more convenient. Excess of chlorine is removed by adding to the water a little photographer's "hypo", about twenty crystals to a gallon.

## CHAPTER V

### THE ATMOSPHERE

OF the four so-called "elements" as known to the ancients—earth, air, fire, and water—air is certainly our special sphere of influence. It is true that, so far as our bodies are concerned, we came from the earth, are sustained by the earth, and return to the earth; but it is no less true that, but for the life-giving qualities of the atmosphere, inhaled in every breath, our stay upon the earth would be short indeed.

Originally deemed an elementary body, air has been resolved into various gases by the simple process of presenting it to bodies which have a greater chemical affinity for one constituent than for the others. Thus, in the well-known experiment, a piece of phosphorus burning in a bell-jar over water unites with the oxygen of the enclosed air, forming a white oxide of phosphorus which dissolves in the water, and leaving behind four-fifths of the air in the form of a gas called nitrogen, for which phosphorus has no special affinity. Again, air may be passed slowly over red-hot copper turnings with much the same result; the copper unites with the oxygen, forming a black oxide of copper, and the other gases of the atmosphere come off unaffected. On the other hand, if a large "empty" bottle be shaken up with about a tablespoonful of lime-water in it, the latter will turn milky, owing to chemical action between the lime and another gas in the air called carbon dioxide or carbonic-acid gas, resulting in the formation of carbonate of lime or chalk. After removing all the oxygen, and carbon dioxide, leaving only nitrogen, and then subjecting this to the action of red-hot magnesium, which will combine with it to form solid magnesium nitride, very small quantities of quite inert gases remain. The most abundant of these is argon, thus confirming the belief, held

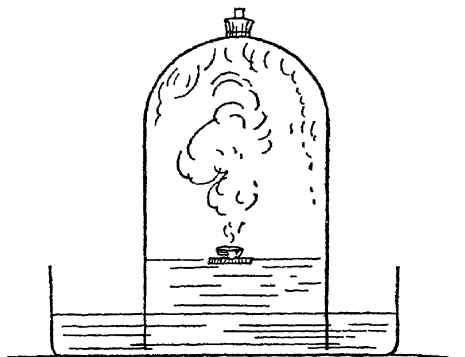


FIG 5.—COMBUSTION OF PHOSPHORUS IN AIR.

since the days of Cavendish, that atmospheric nitrogen was not altogether an element. The analysis of air shows the following average composition :—

	By Weight.	By Volume.
Nitrogen . . . . .	75.51	78.03
Oxygen . . . . .	23.15	20.99
Inert Gases . . . . .	1.30	0.95
Carbon dioxide . . . . .	0.04	0.03

The Inert Gases are made up as follows :—

Helium . . . . .	0.005	} per 1000 vols. of air.
Neon . . . . .	0.018	
Argon . . . . .	9.33	
Krypton . . . . .	0.001	
Xenon . . . . .	0.0001	

The amount of carbonic acid varies from 0.02 to 0.05, or even 0.06 per cent., increasing at the expense of the oxygen. Besides these gases, pure air always contains a variable amount of water vapour, and traces of ammonia, organic matter, ozone, sodium salts, especially near the sea, and other mineral matters. In the neighbourhood of manufacturing towns the air is often very impure, con-

taining, besides dust, appreciable quantities of acids, especially nitric and sulphuric, the latter derived mainly from the sulphur always present in coal. These acids, in conjunction with atmospheric moisture, soon corrode unprotected metallic surfaces, and even the stonework of buildings.

In spite of the fact that the composition of air is so uniform, air is not a chemical compound of these gases, but only a mechanical mixture. The variations, though slight, violate a most important law of chemical affinity to the effect that the same substances always combine in certain fixed and definite proportions, and when the same substances are capable of uniting in more than one proportion, these proportions always bear to one another a very simple numerical ratio.

Nitrogen, which forms four-fifths of the bulk of air, is a very inactive gas, and its sole function in air seems to be to dilute the oxygen and render it breathable. While nitrogen itself is very inert, two of its compounds are very active in their own way, nitric acid or aquafortis being a powerful acid, and ammonia an equally powerful alkali. The compounds into which nitrogen is forced to enter are often very unstable, separating into simpler forms often with extreme violence, and advantage is taken of this instability to form numerous high explosives, of which nitroglycerine or dynamite may be taken as a sample.

Oxygen is beyond doubt not only the most important constituent of the atmosphere, but also of the known earth itself with all that it contains. About one half of the solid crust of the earth consists of oxygen, chiefly combined as oxides in silica and alumina; water contains eight-ninths of its own weight of oxygen, while in the organic world of plants and animals the proportion is nearly as high, from three-quarters to four-fifths; so that oxygen figures as by far the most abundant element in the earth, constituting as it does from two-thirds to three-fourths of the entire globe.



Oxygen may readily be made by heating certain substances which are rich in this element and part with it readily when heated. Common nitre or saltpetre, either nitrate of potash or nitrate of soda, is fairly rich in oxygen, as may be seen by the increased combustion which ensues when some saltpetre is thrown on the fire; and nitric acid and nitrates generally are good oxidisers. But the chief supply of oxygen is obtained by heating chlorate of potash or black oxide of manganese, either separately or by preference together, and the gas which comes off is collected over water. Oxygen may also be obtained from water by decomposing the liquid by means of an electric current, the method of electrolysis, analysing by electricity. As described on p. 54, oxygen comes off at the electrode at which the current enters the liquid, whilst hydrogen separates where the current leaves the liquid. This method produces both gases in a very pure state and is widely adopted where power is cheap. Oxygen may also be produced from air by Brin's process. There is a substance like lime called barium oxide or baryta, which on being heated gently takes up more oxygen from the air, but on being heated more strongly or heated under a diminished pressure it gives off again this captured oxygen, and returns to its original state, and is thus ready to enter upon a second round of duties as oxygen-carrier. The gas thus produced is nearly always mixed with a little nitrogen, but is generally sufficiently pure for most chemical purposes. It is compressed into steel cylinders at a pressure of about 1800 lb. per square inch, and has numerous industrial applications—as, for instance, oxy-acetylene welding.

Oxygen now available commercially in cylinders is produced from liquid air by fractional distillation. Air is compressed to about 200 atmospheres, cooled and suddenly expanded into an insulated chamber. This expansion produces a further drop in temperature, which causes the air to liquefy when about  $-190^{\circ}$  C. has been reached. Liquid air consists of a mixture of

liquid oxygen and liquid nitrogen in about the same proportions as in the atmosphere. Of these two liquids the nitrogen is the more volatile and so it boils off first,

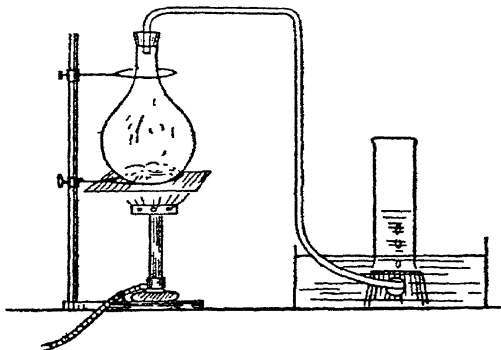


FIG. 6.—PREPARATION OF OXYGEN FROM MANGANESE DIOXIDE AND POTASSIUM CHLORATE.

leaving the oxygen, which is in its turn evaporated and compressed into cylinders.

Although of no commercial importance, there is a natural process of making oxygen which is of great economic value, and which may possibly solve the prob-

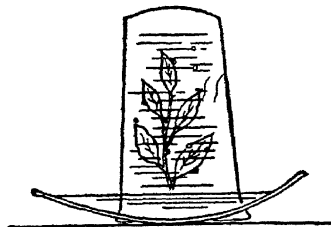


FIG. 7.—FORMATION OF OXYGEN BY PLANTS.

lem of a possible exhaustion of oxygen which once troubled the dreams of too-prudent philosophers. If a sprig of mint be placed in a tumbler filled with water and the tumbler be inverted over a saucer also containing water—a miniature pneumatic trough, in short—bubbles of gas will be seen forming on the leaves when the whole is exposed to sunlight. When these are collected and examined they prove to be oxygen gas, thus showing that green plants in presence of sunlight are able to break up the carbonic acid present in water or air and liberate its oxygen. In this way the action of chlorophyll, the green colouring matter of plants, is in exact antagonism to that of animals, most of which abstract oxygen from the air and give off carbonic-acid gas and other oxides in exchange. Even the purest air contains small quantities of carbonic-acid gas—from three to four parts in 10,000—but by breathing in and out through two different tubes containing lime-water (see Fig. 8), it is easy to see that the air expired contains much more carbonic acid than that inspired; in fact, a hundred times as much. By breathing against a cold surface, like a pane of glass, it is equally easy to show that expired air contains a great deal of water vapour, however dry the atmosphere may be, and altogether there are several important differences between inspired and expired air, as shown in the following table:—

AIR.			
		(Inspired.)	(Expired.)
Nitrogen	. . .	79.00%	79.02%
Oxygen	. . .	20.96%	16.158%, loss $4\frac{1}{2}\%$
Carbonic-acid gas	. . .	0.04%	4.42%, gain $4\frac{1}{2}\%$
Water	. . .	variable	saturated
Temperature	. . .	variable	almost blood-heat, 36°-37° C.
Dust	. . .	always present	always absent

When a vesta or wooden match is burned and the products of combustion are collected in a test-tube, water is formed, as evidenced by the formation of dew on the tube,

and carbonic-acid gas, as will be seen on shaking up the gaseous contents of the tube with a little lime-water. That is to say, the processes of animal life have very much the same effect on the atmosphere as the combustion of ordinary fuel—namely, the withdrawal of some of the oxygen and the substitution of carbonic-acid gas and water. In course of time the proportion of carbonic-acid gas would rise so high as to render the atmosphere unbreathable, and animals would perish from this earth, choked by their own excreta. It is here that plants come in as complementary factors in the economy of nature. By some mysterious chemistry of

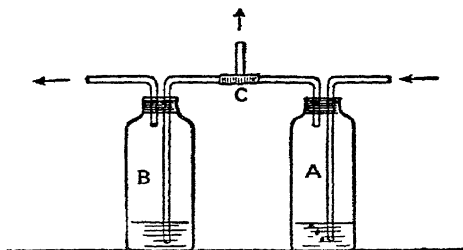


FIG. 8.—CARBONIC ACID IN INSPIRED AND EXPIRED AIR.

A, Bottle with lime-water for inspired air; B, bottle for expired air; C, T-piece for breathing

their own they take these excreta—carbonic acid, water, ammonia, and the rest—and out of them build up plant tissue, liberating oxygen and storing up, in the form of starches and sugars, fats and proteins, those organic forms of nutriment which we cannot create, but must consume.

Generally speaking, the more active life is, the more carbonic acid there will be produced; and the more fuel or carbonaceous matter, the higher will be the percentage of carbonic acid in the air, increasing at the expense of the oxygen.

C (Chemistry)

## CHAPTER VI

### OXIDATION AND COMBUSTION

It has already been seen that when phosphorus, or any other combustible substance, is burned in any confined space, the oxygen of the air is used up to form an oxide of the substance, while the nitrogen remains. Very striking results are obtained when pure oxygen gas is used instead of air. Substances like phosphorus, which burn brilliantly in air, burn with dazzling brilliancy in oxygen; sulphur and charcoal, which burn but feebly in air, burn with great vigour in oxygen (anyone who has seen an oxy-acetylene welder at work will recall the brilliance with which the sparks of molten iron burn); iron wire, which can hardly be said to burn in air at all, gives a miniature pyrotechnic display when burned in oxygen; and, generally speaking, combustion is very greatly increased by the use of oxygen, and still more if the oxygen be at high pressure. In every case an oxide is formed: some solid, as with iron and phosphorus; some gaseous, as with sulphur and carbon; some liquid, as when hydrogen gas burns in oxygen to form water, though in most cases the high temperature produced causes this oxide to form in the state of steam. In all these cases the phenomenon is one of direct chemical union between the substance in question and the oxygen of the air, and it is merely a convention to speak of the latter as a supporter of combustion and of the others as combustible substances. Coal-gas burns in air, yet it extinguishes a lighted taper thrust into it; it is therefore a combustible substance, and not a supporter of combustion. This, however, is merely a popular way of stating the fact that the elements in coal-gas—carbon and hydrogen mainly—have a strong chemical affinity for the oxygen in the air but none at all for the materials of the taper, which, indeed, is also mainly composed of

carbon and hydrogen—another characteristic of chemical action: that two of a trade never agree. By a very simple experiment, air may be induced to burn in coal-gas or in hydrogen, and were our atmosphere composed of hydrogen instead of oxygen, the terms combustible and

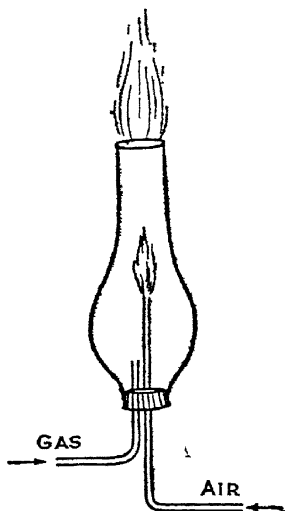


FIG. 9.—COMBUSTION OF COAL-GAS IN AIR AND OF AIR IN COAL-GAS.

supporter of combustion would be reversed. To a chemist combustion is simply the result of direct chemical union, attended by heat, and if vigorous enough, by flame or other visible sign. That a certain temperature is necessary for the production of flame is shown by placing wire gauze over a jet of burning gas. Here the combustible and the supporter of combustion are both present, and flame is actually produced below the gauze;

but since the heat produced is rapidly conducted away by the wire, no flame is formed above the gauze till the latter gets red-hot, when the flame strikes through. This is, of course, the principle of the Davy lamp, used as a safety-lamp in mines. The wire gauze of the lamp allows fire-damp to enter, and a slight explosion may occur within the lamp, but the flame is unable to pass out so as to ignite the inflammable gases outside. The fact that a

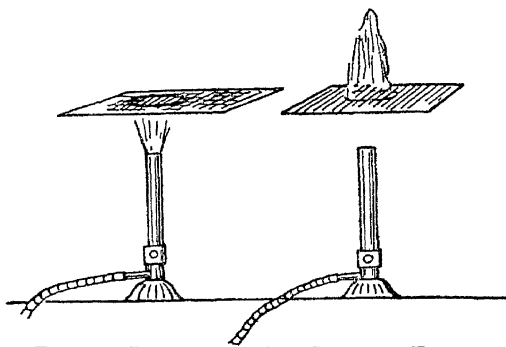


FIG. 10.—EFFECTS OF WIRE GAUZE ON FLAME.

certain minimum temperature is required for combination finds application in the "flash-point" of mineral oils. Paraffin oil is practically a mixture of hydrocarbons, substances containing hydrogen and carbon, both of which elements are ready to unite with oxygen should occasion offer. When some paraffin oil is heated in an open vessel over a burner protected by wire gauze to keep the actual flame from reaching the vapour, at a certain temperature the oil bursts into flame, and this constitutes the "flash-point" as determined by an "open" test. Some of the more dangerous American oils may actually flash in the heat of a summer's day.

The term combustion is capable of extension to chemical

combinations, though these are unattended by smoke or flame. Animal heat is a case in point. We take in oxygen by the mouth and lungs, and combustible substances in the form of food by the mouth and digestive canal; and as a result of our vital processes various waste products are given off—water vapour and carbonic acid, urea and other nitrogenous products, while the body is further maintained at “blood-heat” summer and winter. A gardener takes advantage of slow oxidation when he prepares a hot-bed. Here there is a quantity of decaying animal and vegetable matter ready to combine with oxygen, and assisted in doing so by bacteria of putrefaction, with the result that fermentation sets in—chiefly oxidation by means of living agencies—and a fair amount of heat is generated. In the case of hay which has been prematurely stacked, the heat generated may encourage more rapid oxidation, and thus by a cumulative action end in setting the stack on fire.

Certain vegetable oils, such as linseed oil, slowly oxidise in air with the evolution of heat. If this heat has opportunity to escape, all is well; but if, for instance, rags wet with linseed oil are stacked in a confined space, the heat is conserved, and a fire may break out and quickly gain a hold.

Since chemical action is generally more complete when the combining substances are in intimate contact, it is natural that many substances which are quite safe in their ordinary state may become dangerous when finely powdered. Charcoal shows no tendency to unite with oxygen except at a fairly high temperature, but finely-powdered carbon—say, coal-dust in a mine—may be oxidised at a comparatively low temperature. If the carbon or coal-dust is diluted with some inert substance, the danger of combustion or explosion is greatly reduced. It is now the practice to strew finely-powdered wet slate in mines to dilute the coal-dust, and so diminish the risks of explosion. If a narrow glass tube be sealed at one end, then filled with tartrate of lead and slowly heated



till the contents are carbonised, then on being shaken out the particles of carbon take fire. Not only does this find application in dusty coal-pits, but also in flour- and cotton-mills, where the air is loaded with dust of a highly combustible nature; and in these places the dust has either to be kept down by watering or removed by ventilating fans or similar appliances.

The principles of combustion are seen in the manufacture of gunpowder. This contains charcoal as its combustible substance, with a little sulphur to start and maintain the action; but as charcoal does not readily oxidise of its own accord, more especially in the confined space of a gun-barrel, an oxidising agent is supplied in the shape of saltpetre. The finer the grains the more rapid is the oxidation and the more severe is the sudden strain produced upon the gun; hence for big guns the grains were very coarse, increasing in size with the calibre of the gun, so as to produce a cumulative explosion and give the ball a continuous shove rather than a single impact. The products of explosion are mostly gases, steam, carbonic-acid gas, and nitrogen compounds, but a serious objection to common gun-powder is the smoke, chiefly potassium sulphide and sulphate, which not only fouls the barrel, but also reveals the whereabouts of the firer. To obviate these objections "smokeless powders" are universally used, the intention being to produce a substance which on oxidation gives nothing but gases. Most of these are organic substances like cellulose and glycerine, treated with nitric acid or some other oxidising agent instead of solid saltpetre, and thus forming explosives like nitro-cellulose or guncotton and nitroglycerine or dynamite respectively. Thin tissue-paper, which is practically cellulose, will explode if struck smartly with a hammer on an anvil. Some of these modern explosives will be discussed in Chapter XIII.

When iron wire is burned in oxygen, or when iron sparks burn in a foundry, the oxide of iron produced is black and magnetic, having the same composition as

natural lodestone. When iron is left to combine slowly with air it rusts, forming a brown oxide, practically identical with yellow and brown hæmatite ore on the one hand, and with rouge on the other. The same substance may thus form different oxides, but the proportion of oxygen in each can always be expressed by a simple numerical ratio. Heat is evolved when iron rusts, as well as when iron is burned in pure oxygen, only in the latter case the action is all over in a few minutes, whereas rusting may be a matter of weeks, and the rise of temperature in such a case is too gradual for notice.

This corrosion of the iron by the atmosphere can be prevented if access to its surface is denied to the air by providing some protective covering which adheres strongly. The protective coating may take the form of a layer of varnish, paint or lacquer, or else a thin film of another metal such as nickel or chromium. These thin films are usually produced by electro-plating. In each case the protective film, whatever its form, will only adhere properly and prevent corrosion if it has been applied to a clean surface of the metal. All traces of scale, oxide or grease must therefore be most carefully removed before plating is commenced.

Careful investigation shows that many oxidising actions cannot take place in the total absence of moisture. Only a trace of water-vapour is necessary, and if this is lacking either combination does not take place at all, or else proceeds very slowly.

The oxidation of iron is not as straightforward as the beginning and end products lead one to suppose. Rusting takes place only in moist air, and then only when a trace of carbon dioxide is present.

If oxygen is very carefully dried, it will not combine with either sulphur or phosphorus; it is even possible to distil these elements in the dry gas. Similarly, sodium and potassium scarcely react at all with dry oxygen. Carbon combines with dry oxygen only very slowly, even on heating. A mixture of carbon monoxide

and oxygen, which normally requires only a small spark to explode it, when dry will need a powerful electrical discharge to "touch off" the reaction.

Certain other reactions, it is interesting to note in passing, are slowed down or stopped entirely in the absence of water. For instance: dry chlorine does not combine with metals, except mercury. Dry ammonia and dry hydrochloric acid gas only mix, but do not combine to form ammonium chloride.

## CHAPTER VII

### CARBON AND ITS OXIDES

MOST if not all the combustible substances used as fuel consist of carbon or carbonaceous materials, and since animal heat is the outcome of the slow combustion of food-stuffs, these also may be included under the term fuel. Carbon itself is an element—that is, a substance which has hitherto not been decomposed—and it does not occur free in nature except in two mineral forms: graphite, also known as plumbago or black-lead, and diamond. Soot may be looked upon as impure carbon, while lampblack, the purer soot obtained by burning heavy oils, is well known as a pigment. To these must be added the different kinds of charcoal, obtained by heating in a confined space any carbonaceous substance whatsoever, such as bones, wood, or coal. Bone charcoal or animal charcoal has a most remarkable power of absorbing gases and removing colouring-matters, and on this latter score it is regularly used in sugar-refineries in order to clarify sugar. A piece of bone charcoal will absorb more than eighty times its own bulk of ammonia gas, and a similar action occurs with drain gases, these latter being not only absorbed but also rendered harmless. Another form of charcoal which is extensively used where great powers of absorption are required is that made from the shells of coco-nuts; it is used in respirators and gas-masks, or wherever gases must be removed by absorption. Gas coke, the charcoal obtained from common coal in gas-works, is now very largely employed in filtering sewage, and compressed carbon blocks are also used in domestic filters for drinking-water. Foundry coke is made from coal by heating in suitable ovens to which only a limited supply of air is admitted. During the coking process many by-products are given off, such as tar, ammoniacal vapours, and gases of various kinds—

in short, the whole process resembles very closely that of making coal-gas. Ivory-black or bone-black is a pigment formed by grinding down bone charcoal. Graphite or black-lead fills an important niche in the industrial world, being extensively used for lead pencils, for polishing grates, for crucibles, either alone or mixed with fire-clay, in connection with smelting metals, for electric lamps of the arc pattern, and lastly, in the form of powder, as a lubricant where oils are unsuitable. The properties and uses of diamonds are too well known to require mention. Many diamonds, by reason of defects of colour or structure, are unsuited for jewellery, but they are of the utmost value in cutting and polishing precious stones and even, in the form of a diamond drill, for rock-boring and other mining operations.

In industry, diamonds are used for glass-cutting and for machining hard and tough metals. A soft iron disc, its edge charged with diamond dust, acts as a glass saw. Tools for turning and boring tough metals, at high speed, may be provided with cutting tips made from diamonds. The dies through which fine wires are drawn are made from diamonds, so that the hole will not enlarge as a result of wear.

Carbon thus presents the curious phenomenon of an element capable of appearing under widely different physical forms. All these varieties are identical in chemical composition and behaviour, yet they vary in appearance, specific gravity, power of conducting heat and electricity, power of combining with oxygen, and so on. This phenomenon is known as allotropy, and carbon shares the possession of allotropic forms with oxygen, sulphur, phosphorus, silicon, and many other elements.

Since diamond and graphite are simply allotropic forms of carbon, many attempts have been made to form them artificially. In making cast-iron and steel, graphite scales are often formed as the result of the separation of carbon originally present in the form of charcoal. Under the great heat and pressure of a blast-furnace the melted

metal actually dissolves a certain proportion of charcoal, but often re-deposits some of this in cooling, in the form of graphite scales. Again, in the retorts used in making coal-gas there is often found an internal coating of artificial graphite known as gas carbon, arising from the decomposition of hydrocarbon gases within the retort. Given conditions of slow cooling under sufficient pressure, it should not be impossible to produce artificial diamonds from, say, lampblack, or other form of charcoal. These conditions, however, were difficult to find, and though the discovery of artificial diamonds dates from 1880, and despite the expenditure of considerable sums of money by ingenious investigators, artificial diamonds have never been produced in either commercial quantities or quality good enough for use as gems. Moissan, a French chemist, produced diamonds by carbonising sugar under great heat and pressure, thus encouraging the formation of carbon crystals, and the necessary pressure is produced by making use of a property of iron. It is well known that water is an exception to the general law of expansion under heat, since it expands when freezing, ice being bulkier than the water from which it was made. This property is shared by other substances, and among these by iron. Melted iron confined in a strong steel case tends to expand on solidifying, and since the energy of expansion is unable to rupture the case, the result is a tremendous pressure within the iron itself, affecting any carbonaceous materials present.

Like nitrogen, carbon seems to be intimately associated with life, and there is a possibility that even such forms as graphite and diamond may be of organic origin. An interesting series is indeed presented by the carbonaceous rocks, in which the proportion of carbon steadily increases up to the maximum. The first link in such a chain would be supplied by growing plants, in which the total percentage of carbon rarely exceeds 40, then come the different kinds of peat, spongy and compact, in which vegetable features are still predominant, though there is

much less water and between 50 and 60 per cent. of carbon. Then comes lignite or brown coal, almost resembling fossil wood and already assuming a mineral aspect, seen to perfection in jet, which is metamorphosed lignite. When the percentage of carbon reaches 80, the result is coal, and here the series is finely graded, from the soft bituminous Scotch coals through splint coal and steam coal up to smokeless coal or anthracite, in which there may be as much as 95 per cent. of carbon. The following table shows how the proportion of carbon increases, at the expense of the volatile matter (such as hydrocarbon gases, carbon dioxide, hydrogen) and moisture. The proportion of "fixed" carbon is less than the total carbon present initially owing to loss of these volatile carbon compounds during the process of transformation of vegetable matter into coal.

	Ash	Fixed Carbon.	Volatile Matter.	Moisture.	Calorific Value. B.Th.U./lb.
Wood . . .	1.5	25.0	53.5	20.0	7,400
Peat . . .	1.2	29.2	51.5	18.1	9,900
Lignite . .	8.0	43.1	42.7	6.2	11,700
Bituminous Coal . .	6.3	63.5	29.2	4.0	14,950
Anthracite .	5.4	86.5	6.1	2.0	15,720

Very often a seam of coal passes into a kind of anthracite, or even a natural coke, owing to the presence of an intrusive dike of igneous rock, which in the molten condition supplied sufficient heat and pressure to effect the metamorphosis. Lastly, in graphite and diamond the metamorphosis is complete; even the former betrays to the microscope no traces of its vegetable origin, and in diamond the purely crystalline stage has been reached as the final product of two great natural forces, heat and pressure, acting together and acting continuously.

When carbon or anything containing carbon is burned in plenty of air, carbon dioxide, popularly called carbonic-acid gas, is formed, and this gas is readily recognised by

the facts that it extinguishes a light and turns lime-water milky, forming carbonate of lime. This is the gas always found in mines after an explosion, and it is called by the miners after-damp, black-damp, or choke-damp, because it not only refuses to support combustion, but is unable to sustain life. Air containing more than 1 per cent. of carbonic acid is distinctly unfit for breathing, though it will easily support combustion, and since this gas is given off as a waste product in the breath, means must be taken either to remove it or to dilute it largely with fresh air. From the comparison of inspired and expired air given on page 64 it will be seen that the proportion of carbonic acid in the latter is increased more than a hundred-fold.

Besides being formed by the combustion of carbon, this gas is produced in a state of great purity under the fermenting action of yeast, and in a great many breweries arrangements are now made whereby the gas is recovered from the brewing-vats and used in the manufacture of aerated waters. A third method of forming carbonic-acid gas is by expelling it from its compounds, called carbonates, by means of almost any acid (see equation on p. 22). The carbonate generally used in domestic circles is baking-soda, which is bicarbonate of soda, and the acid is usually tartaric acid in crystals. In home baking, however, other acid substances are used, such as butter-milk, which contains lactic acid, cream of tartar, which is acid tartrate or bitartrate of potash, and so on. It is important to observe that, whereas yeast leaves no residue in baking, these chemical substances form new combinations which remain in the bread. Thus tartaric acid and baking-soda give carbonic-acid gas, but they also form tartrate of soda, which remains behind. If cream of tartar be used instead of tartaric acid, the residual product is the double tartrate of soda and potash familiar under the name of Rochelle salt. On the manufacturing scale for use in aerating water this gas is usually obtained by the action of dilute hydrochloric



acid upon marble. This substance is one of the many forms of carbonate of lime and, as in the carbonaceous rocks, an interesting series may be obtained, starting from the shells of the living animal, through shell limestone, coral limestone, and chalk, up to limestones in which all traces of shell structure have disappeared, and so to marble, a metamorphic or altered limestone, and

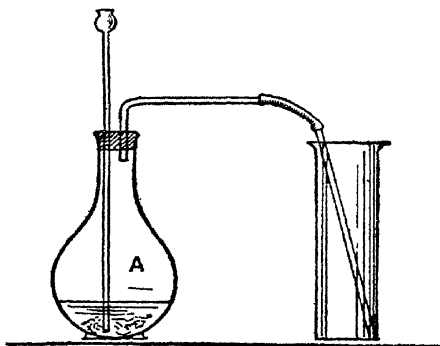


FIG. II.—PREPARATION OF CARBON DIOXIDE.

A, Flask with marble chips and hydrochloric acid.

finally calcite and Iceland spar, the purely crystalline form. Of recent years aerated waters have been carbonised by the use of compressed carbonic-acid gas recovered from breweries and stored under pressure in steel cylinders. By increased pressure the gas may be liquefied and even frozen, solid carbonic acid resembling flakes of snow. Solid carbon dioxide is much used as a refrigerant in preference to ice because it is dry, leaves no mess, gives a lower temperature and is more economical. When compressed, it forms a hard, ice-like mass, and is marketed under the trade name of "Drikold". One popular and familiar application is to be seen all over

the country wherever ice-cream bricks are sold. These may be kept for some considerable time in perfect condition, thanks to the reduced temperature which solid carbon dioxide creates. The name "soda water", as usually applied, is a misnomer; such water rarely contains anything except an over-charge of carbonic-acid gas. True soda water contains, in addition, a little carbonate of soda in solution, just as potash water contains carbonate of potash or pearl ash. Most effervescing drinks, such as beer, champagne, lemonade, owe their

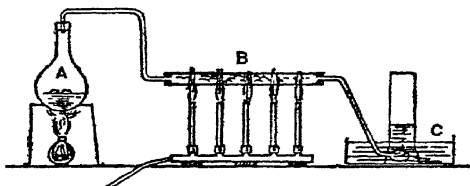


FIG. 12 — APPARATUS FOR "WATER-GAS".

A, Flask to generate steam; B, gun-barrel with charcoal, heated by bunsen burners; C, pneumatic trough.

sparkling character to this gas, produced by fermentation, as in beer and wine, or chemically as in most aerated waters and health-salts.

When a fire is burning low there may often be seen a blue or purple flame playing above the red-hot embers. This is the combustion of carbon monoxide or carbonic oxide, another compound of carbon and oxygen but containing only half as much oxygen as carbonic acid. It is always produced when charcoal or coke burns in an insufficient supply of air, and hence is always present in the heart of a fire; on reaching the top of the fire, however, where plenty of air is to be had, the carbon monoxide doubles its proportion of oxygen and burns with a blue flame, forming carbonic-acid gas. It is also formed along with hydrogen in "water-gas" when steam is passed over red-hot coke, an experiment

which may be done with a gun-barrel filled with charcoal and heated red-hot. It is a very poisonous gas, one part in 1000 parts being injurious to health. This is the gas which causes death in so-called charcoal and coal-gas poisoning, for coal-gas contains a great deal of carbon monoxide. In closed iron stoves, such as are commonly used in America and on the Continent, this gas is sometimes productive of danger, for it is produced in great quantity within the stove, and when the iron gets red-hot, this carbon monoxide is absorbed by the hot surface and given off into the air of the room by the cooler surface. Many hot metals have the power of thus absorbing or occluding gases and parting with them again on cooling, and cast-iron is among the number.

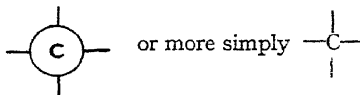
Carbon monoxide is a particularly dangerous poison because its action is cumulative. In the lungs the blood comes into contact with the air which we breathe, and the red corpuscles, which contain hæmoglobin, are the oxygen-carriers. Carbon monoxide combines much more powerfully with hæmoglobin, forming carboxy-hæmoglobin, than does oxygen which forms oxy-hæmoglobin. In consequence, the blood cannot supply the body with the oxygen which it needs, and so the tissues are gradually poisoned.

Users of domestic gas will know that it is sold to them by the "Therm", which is a measure of the heat-value of the gas. One Therm is equivalent to 100,000 British Thermal Units (B.Th.U.). One B.Th.U. is the amount of heat required to raise 1 lb. of water through 1° F. The incandescent gas mantle superseded the open burner and laid additional emphasis on the value of gas for heating. With the addition of water-gas to coal-gas, in varying amounts, it became increasingly difficult to fix the cost of the gas used, solely in terms of its volume when the real basis was its calorific value. A legal standard was accordingly laid down in which the calorific value must not fall below a certain level per 1,000 cubic ft. of gas consumed. Hence, we now pay for gas

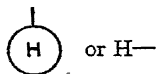
in terms of the heat we can get from it, and not solely on the basis of how much space it occupies.

Gas poisoning is nowadays more dangerous on account of the high proportion of carbon monoxide in domestic gas. This is derived from water-gas, which is added in order to give greater heating value. When burnt, the flame is almost non-luminous, and so a small amount of oil gas is added to impart luminosity to the flame. This is derived from crude oils, which are "cracked" in special producers in order to give the necessary oil gas.

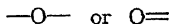
Carbon offers an interesting illustration of the atomic theory in chemistry. Just as oxygen combines with other substances in multiples of 16, so carbon combines in multiples of 12, and the smallest conceivable particle of carbon capable of entering into combination may be be figured as a circle with four arms, thus :—



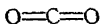
and having a weight of 12. Similarly, hydrogen may be figured as a circle with one arm—



and having unit weight; oxygen thus :—



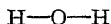
with a weight of 16. In forming carbonic-acid gas one atom of carbon unites with two atoms of oxygen, so that the formula of this gas is  $\text{CO}_2$ , or pictorially—



in which the carbon is saturated with oxygen or has combined with oxygen to the full extent of its powers. This is expressed numerically by the formula  $\text{CO}_2$ , which also tells that 12 parts of carbon by weight have combined with twice 16 or 32 parts of oxygen gas. In carbon monoxide, on the other hand, 12 parts of carbon are in combination with only 16 of oxygen, half the full quantity, so that this gas is quite ready to take up another "atom", or 16 parts of oxygen. The formula of carbon monoxide is thus  $\text{CO}$ , or pictorially—



in which two arms of the carbon are still uncombined. In the same way water, which is composed of 16 parts of oxygen to 2 parts by weight of hydrogen, is represented by the formula  $\text{H}_2\text{O}$ , or—

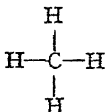


whereas the combination—



is still unsaturated and therefore unstable, being ready to combine with more hydrogen or its equivalent. Since hydrogen has the lightest weight of any known substance, and also the smallest combining power or equivalence, it is generally taken as unity; a cubic foot of oxygen is, however, 16 times as heavy as a cubic foot of hydrogen, and as the number of atoms in a cubic foot is supposed to be the same, the only way out of the difficulty is to suppose that an atom of oxygen is 16 times the weight of an atom of hydrogen. Since all gases expand equally under heat,  $\frac{1}{273}$  of their bulk for every degree centigrade, it is assumed that the number of atoms in a cubic foot of each is the same, otherwise their rate of expansion would be unequal.

When the four-armed atom of carbon is saturated with one-armed atoms of hydrogen, thus :—



or  $\text{CH}_4$ , the substance symbolised is a well-known gas called marsh-gas, fire-damp, light carburetted hydrogen or methane, one of the constituents of coal-gas, and the first of a numerous series of bodies called paraffins. Another carburetted hydrogen, ethylene, is represented by  $\text{C}_2\text{H}_4$ , and these along with carbon monoxide and hydrogen constitute the bulk of coal-gas.

When coal is distilled in a retort, as in gas-making, solid coke and gas carbon are left in the retorts, while a great many volatile products are liberated and pass over. Some of these are heavy vapours which readily condense, forming tar and water; others are gaseous impurities which are very soluble in water and are therefore easily removed by washing, like ammonia and sulphuretted hydrogen; others, like carbonic-acid gas and carbon disulphide, are removed by treatment with freshly-made quicklime, and the rest constitute coal-gas as supplied for house use. This is essentially a mixture of hydrogen, carbon monoxide, and several hydrocarbons, such as methane and ethylene, already mentioned, with possibly a little nitrogen introduced from the air or liberated in the process. In spite of careful purification, coal-gas always contains a little sulphur, generally in the form of carbon disulphide, and hence when gas is burned sulphur compounds are always formed and among them sulphuretted hydrogen. The sulphur content of domestic gas is, however, very carefully regulated and must not exceed certain statutory limits (0.00001%  $\text{H}_2\text{S}$ ).

This objection does not apply to oil-gas, once so much used in lighting railway-carriages. The oils from which

the gas is distilled are all hydrocarbons, containing hydrogen and carbon only, and consequently on burning they yield nothing except water and carbonic-acid gas. When a candle flame or a gas flame from a rat-tail burner is examined, it is seen to consist of two distinct zones : an inner dark cone, perfectly transparent, and an outer luminous cone where the light is brightest. By holding



FIG. 13.—STRUCTURE OF A FLAME.

A, Core of unburned gas; B, luminous or "reducing" flame; hydrocarbon in excess; C, non-luminous tip or "oxidising" flame, oxygen in excess, greatest heat.

a piece of cardboard across such a flame at different levels, cross-sections of the flame may be obtained in the form of a series of charred rings, generally smoked as well. The dark centre is thus shown to consist of unburned gas, and by means of a fine glass tube some of this gas may be led out and burned. The luminous mantle surrounding the central cone has long been matter of discussion, some authorities maintaining that the luminous

osity was due to the presence of white-hot particles of solid carbon derived from the gas, others maintaining that the combustible matters were entirely in the condition of vapour. When combustion is complete—that is, when there is excess of air or oxygen—the flame is very hot, dark blue, and non-luminous, as may be seen by the blow-pipe. When, however, there is lack of air, the flame becomes luminous and smoky, depositing solid carbon on any cool object held in it. Such a flame contains excess of carbon and hydrogen, both ready to combine with oxygen, and hence it is known in blow-pipe work as a reducing flame, since it abstracts oxygen from substances heated in it. In the common gas-burner two jets of gas flatten each other out into a thin sheet, so as to give a fairly good air supply, but there is still a large blue centre of cool, unburned gas. If the air be heated as in regenerative burners of the Siemens type, sometimes used in shops, this blue portion disappears, giving increased luminosity. A similar result is obtained in argand burners, which have a cylindrical flame assisted by a chimney draught. A common bunsen burner burns a mixture of gas and air, the latter in excess, so that the flame is oxidising, non-luminous, but very hot. When the air-holes are closed, the ordinary flickering, smoky flame appears. Occasionally through lack of pressure, as when the gas is turned down, the flame in a bunsen “lights back”, producing the unpleasant and indeed poisonous fumes of acetylene gas. This may be avoided, and in ordinary gas-burners is avoided, by inserting a piece of wire gauze in the body of the burner, on the principle of the Davy lamp. The ordinary bunsen or spirit-lamp flame is non-luminous, but if lycopodium or magnesium powder be blown through it, a brilliant flash is produced, luminous enough for photographic purposes. In the limelight luminosity is obtained by directing a non-luminous but intensely hot blow-pipe flame of coal-gas and oxygen, or, better still, of hydrogen and oxygen, against a cylinder of hard lime. The lime is not burned



at all, but is simply raised to a white heat, glowing intensely, and often partly fused on the surface. This is the principle of incandescent-gas lighting. Over the outer cone of a bunsen flame there is suspended a mantle of cotton steeped in certain salts. When the mantle is ignited the cotton support burns away, leaving a mantle of ash, the oxides of thorium and cerium most commonly, and this behaves like lime, glowing white-hot in the otherwise non-luminous flame. Another application of air-supply in lighting is seen in the "lucigen" and similar lights employed in railway yards and for outdoor work generally. For this purpose heavy oil is used, obtained by distilling tar and unsuited either for lubricating or for burning in a common lamp. By means of a jet of steam or compressed air this oil is blown out in spray, and burns with great brilliancy owing to the increased air-supply and pressure.

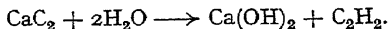
These systems all depend upon the chemical combination of carbon and hydrogen with the oxygen of the air, since even in limelight and incandescent gas-lamps such combination furnishes the temperature required for incandescence. In electric lighting, on the other hand, there is no combustion, and consequently no exhaustion or vitiation of air. When a current of electricity passes through a thin platinum wire, part of the electric energy is converted into heat and the wire glows. A fine carbon thread might be taken instead of platinum, but in this case the glowing carbon would combine with air and speedily be oxidised in the form of carbonic-acid gas; therefore, to prevent such a possibility, the carbon thread is enclosed in a glass bulb from which the air has been removed as far as possible. The filament, as this fine thread is called, is now made of tungsten, a metal with an extremely high melting-point (about  $3540^{\circ}\text{C.}$ ), and is enclosed in a bulb containing an inert gas, such as argon, at a low pressure. The gas helps to prevent the filament from vaporising which it tends to do at temperatures of incandescence. In the

larger arc lamps, used at most railway stations, public streets and in cinema projectors, the principle is the same; the resistance here takes the form, not of a thin thread, but of a small air gap to be bridged between two pencils of graphite, and the electric energy, transformed into heat by this resistance, actually resolves the carbon into incandescent vapour; combustion in the strict sense, there is none, although the carbon vapour burns.

Other electrical sources of light are obtained by discharging high-tension electrical alternating currents through various gases and vapours. Of these the most familiar is the "neon sign", the red glow of which results from the electrical excitation of the rare gas neon contained in glass tubes at a very low pressure. If the gas helium is used instead, the light emitted is blue, and by altering the composition and pressure of the gases in the tubes, the colours produced can be changed.

If, instead of an inert gas a metallic vapour is used, a light of still different colour can be obtained. When mercury vapour is excited under high pressure it gives out a blue-green light which is familiar in many parts of the country where special anti-dazzle systems of street lighting have been installed. On the other hand, sodium vapour produces an intense golden-yellow light having remarkable penetrating properties.

Acetylene gas ( $C_2H_2$ ), already mentioned as being formed when a bunsen burner lights back, is now made on a large scale by simply allowing water to act on calcium carbide ( $CaC_2$ ). This substance is made by heating together in an electric furnace a mixture of coke and chalk, or calcium carbonate, and under the action of water it forms slaked lime and acetylene:—



The gas is a powerful illuminant, a No. 5 burner giving a light of 240 candle-power. It has a strong action on copper and brass, so these metals cannot be used for

storage or fittings in using acetylene gas. In addition to its use for illumination, it is used industrially in conjunction with oxygen for welding and cutting steel and other metals. The oxy-acetylene flame gives intense heat and easily melts many metals. As the intense heat can be applied locally, joins can be made and sealed by welding. For cutting steel the flame first heats the part to be cut until it is white hot, and then the oxygen jet completes the cut by burning the metal away by oxidation. By this means thicknesses of metal can be readily cut which would otherwise be either difficult or impossible, as well as expensive, if cut by mechanical means.

## CHAPTER VIII

### THE DISTILLATION OF COAL

So many important chemical industries have arisen in recent years in connection with the destructive distillation of coal that it is advisable to present a general view of the several processes. When coal, shale, wood, bones, or other organic matters are heated in closed retorts, a solid residue of charcoal is left in these retorts, while

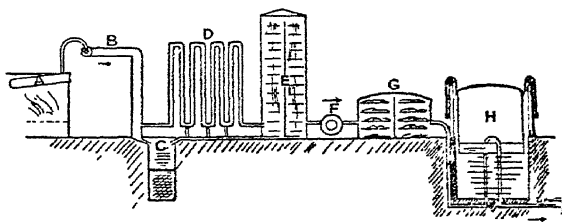


FIG. 14 —DIAGRAM OF GAS-WORKS.

A, Retorts; B, hydraulic main; C, tar-well; D, condensers; E, scrubber or washer; F, exhaust pump; G, lime purifier; H, gas holder.

various volatile products distil over as vapours. Some of these volatile products are permanent gases, such as those found in coal-gas, comprising hydrogen, various hydrocarbons which lend illuminating power, carbon monoxide and dioxide, nitrogen and, in the case of coal, sulphuretted hydrogen. The other volatile products are either gases like ammonia and hydrogen sulphide which are very soluble in water, and therefore easily washed out, or vapours which, on cooling, yield water and tarry liquids. Combinations frequently occur between these by-products, thus some of the carbonic-acid gas combines with the ammonia to form crude carbonate of ammonia,

and in the same way chloride, sulphide, and sulphate of ammonia, and cyanides of all kinds are found either in the tarry liquor or in crude gas. Similar decompositions occur in coke-ovens, and in fact wherever an organic substance like coal or shale is heated in absence of air, and every modern coke-oven is now fitted with elaborate recovery plant to save the ammonia, cyanogen, and furnace gases which were formerly allowed to escape. To

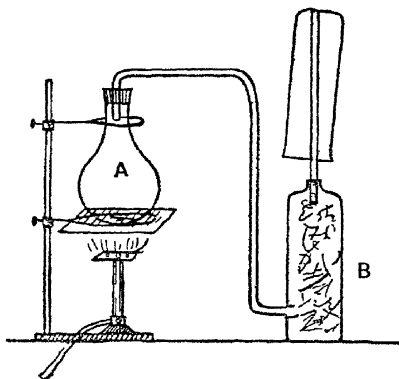


FIG. 15 —PREPARATION OF AMMONIA.

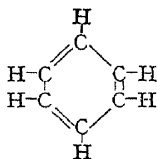
A, Flask with sal-ammoniac and lime; B, drying-tube with lime or calcium chloride.

such an extent has this been the case that the old process of making ammonia by distilling horns—whence its popular name, spirits of hartshorn—is completely obsolete, and at one time the price of these by-products stood so high that many blast-furnaces were run for the sake of the ammonia produced, the iron itself being looked upon as the by-product. The ammoniacal liquor of the gas-works is treated with crude oil of vitriol, or sulphuric acid, and the result of this combination is sulphate of ammonia—a

valuable food for plants. From sulphate of ammonia or from the natural substance sal-ammoniac, which is ammonium chloride, pure ammonia gas is easily obtained by heating with quicklime (Fig. 15), but since this gas is exceedingly soluble in water, it is more conveniently handled in the form of a saturated solution of specific gravity 0.880. The domestic uses of ammonia are many and diverse. It is a powerful alkali, able to neutralise the strongest acids; it readily combines with fats and oils to form soluble soaps, and is thus useful for removing grease, a function which finds wide application, from scouring new blankets to washing the hair. In very dilute solutions it is very good for cleaning glass and silver, while a drop or two of the strong solution inhaled is a powerful stimulant. "Smelling-salts" are simply carbonate of ammonia with or without the addition of some aromatic substance. The best form of ammonia for household purposes is a Winchester quart of the strong solution (sp. gr. 0.880); it should be kept in a cool place with the glass stopper smeared with a little vaseline. Since gases in solution are expelled by heat, it is obviously of little use to add ammonia solution to boiling water, as is often done on washing-day. A very important industrial application of ammonia is to refrigeration. The gas is compressed, cooled, and suddenly allowed to expand through jets; this expansion robs it of its own heat and makes it liquefy owing to the drop in temperature so produced. The cold liquid is circulated through coils and used to cool "brine" (actually calcium chloride solution), which in its turn may be used to freeze water to ice or to cool air. The ammonia circulates continuously through the system with practically no loss; it is simply compressed, cooled and expanded inside a closed system. Other gases such as carbon dioxide may also be used similarly.

Apart from ammonia, the formula of which is  $\text{NH}_3$ , the most useful product of coal distillation is the tar. Tar is a highly complex mixture of substances belonging to

different chemical families. It contains hydrocarbons, of which benzene may be taken as the type; carbolic acid and similar compounds containing carbon, hydrogen, and oxygen; sulphur compounds; nitrogen compounds like ammonia and aniline, the base of the well-known dyes; and lastly, those highly carbonaceous substances which go to form pitch. The separation of these substances is a fine application of "fractional distillation"—*i.e.*, distilling at different boiling-points in succession, beginning with the lowest. In this way the "first runnings" come off at  $105^{\circ}$  C., then the "light oils" up to  $210^{\circ}$  C., then carbolic oil at  $240^{\circ}$  C., creosote oil at  $270^{\circ}$  C., finally anthracene oil and pitch. The first runnings contain ammoniacal liquor, yielding ammonia as before, and crude naphtha, generally worked up with the second fraction or light oils. These are so called because they are lighter than water, and they consist largely of crude naphtha, which under suitable treatment yields common naphtha for burning in lamps; solvent naphtha, a finer sort, free from naphthalene, and extensively used as a solvent for india-rubber; thirdly, xylene and toluene, both used in the dyestuffs industry; and lastly, benzene. This important substance has a formula  $C_6H_6$ , and yields an immense variety of substitution products. The composition of benzene may be represented pictorially as a ring of six carbon atoms, each carrying an atom of hydrogen, thus:—



and in this combination any or all of the hydrogen atoms may be replaced by an equivalent element such as chlorine (Cl), or even by equivalent groups like OH,  $NO_2$ ,

and so on. Thus phenol, commonly called carbolic acid, is represented by the formula  $C_6H_5OH$ , in which OH has replaced an atom of H, while benzene treated with nitric acid yields  $C_6H_5NO_2$ , in which the group  $NO_2$  replaces H, giving nitrobenzene. From this, again, by substituting  $NH_2$  for  $NO_2$  we form  $C_6H_5NH_2$ , aminobenzene or phenylamine, commercially known as aniline oil, and from this, again, by suitable reagents, are formed the whole series of aniline dyes. Some of the commoner benzene derivatives will be dealt with in a subsequent chapter.

The carbolic and creosote oils which form the next fraction in tar distillation are often taken off together under the name of heavy oils, and they contain creosote, carbolic acid, and naphthalene. Creosote is sometimes used as an illuminant in lucigen lamps provided with an air or steam blast, but its chief use is as an antiseptic to arrest decay in wood. Railway sleepers, telegraph posts, piles, and generally timbers intended for use in the earth or water are usually injected with creosote at high pressure, so that the preservative penetrates to every part of the timber. Commercial carbolic acid contains cresol as well as phenol, the latter being pure carbolic acid, used for medicinal purposes. Its appearance and use as a disinfectant are well known, though in this latter respect it is rather an antiseptic, arresting growth, than a positive germicide. It must on no account be taken internally, as it is a powerful and corrosive poison which is most painful in its action, which fact, if more widely known, would surely reduce the tragic number of suicides who make it their last resource. The best antidote in such cases is Epsom salts, sulphate of magnesia, since the carbolic acid combines with these, forming a harmless sulpho-carbolate of magnesia. Since the acid is highly corrosive, some emollient in the form of oil should also be given. The solid crystals of carbolic acid are easily vaporised by heat, and in this way carbolic acid may be used as an aerial disinfectant, like the fumes of burning



sulphur ; but it is generally used in the form of solution, from 1 to 5 parts in 100 of water, according to the work intended.

Naphthalene is another solid obtained from creosote oil. In the form of cakes (moth-balls) it is used as an insecticide instead of camphor, and also for enriching coal-gas. For this purpose a little naphthalene is enclosed in a small case near the burner, the heat from which vaporises some of the naphthalene, which thus mixes with the gas immediately before combustion. It is a useful garden pest killer. Ground which is newly put into service may be cleared of many insect pests by having naphthalene dug into it during the winter, before it is used for raising the first crop. The chief use of naphthalene, however, is to serve as a base for the production of dyestuffs.

Anthracene oil, or green oil, is the last liquid product of coal-tar, and is chiefly valuable on account of containing anthracene, another basis of dyestuffs, especially of alizarin, or artificial madder, used for Turkey-red. The solid residue is pitch, hard or soft, according as the anthracene oil is more or less removed. It is used along with sand for making "asphalt" paving, and hard pitch powdered forms briquettes, a substitute for coal, containing coal-dust and pitch. By still further distillation pitch may be made to yield a heavy pitch oil, leaving a residue of pitch coke.

The table on p. 95 shows at a glance most of the products derived from coal, as well as a few of the more important substances formed from these by simple chemical treatment.

It is well known that of the large variety of purposes for which oil is used the most important is as a fuel of some sort, whether it is for driving motor vehicles or firing the boilers of liners and battleships. Practically the entire world supply of oil comes from petroleum wells in either America or remote parts of Asia and, as the source is a natural one, there is always the danger that the demand, even continuing at its present rate, will soon

Coal yields	Coal-gas			
	Sulphurous vapours	{ Sulphuretted hydrogen Sulphurous acid.....	Sulphuric acid (oil of vitriol)	
	Water			
	Ammoniacal liquor (carbonate of ammonia)	{ + Sulphuric acid = Sulphate of } + Lime = { Ammonia gas ammonia } (Plaster of Paris)		
		{ + Hydrochloric acid = Chloride of } + Lime = { Ammonia gas ammonia } Chloride of lime		
	Coal tar	1st light oils.....	{ Ammonia.... Benzene.....	{ Benzene...Nitrobenzene ...Aniline
		2nd light oils (Crude naphtha)		Toluene Xylene
		Heavy oils.....	{ Creosote..... Carbolic acid..... Naphthalene }	{ Solvent naphtha Burning naphtha
		Anthracene or green oils...	Anthracene...Alizarin (Turkey-red)	
	Pitch....	{ Pitch oil Pitch coke		
	Solid (residue)	{ Gas coke Gas graphite		

exceed the supply unless either some hitherto unknown source can be tapped or some means of manufacturing oil from an existing commodity can be put into operation. As we, in this country, possess few petroleum wells, and as their total output falls far short of requirements, it is particularly important that further "home-made" oil supplies should be available for use in time of emergency. As we have already mentioned, oils of various grades are obtainable by the distillation of coal, but the yield is small and, from the point of view of oil production, the method is a wasteful one. It has been discovered that crude oils can be transformed into light oils by processes known as "cracking" and hydrogenation. The first of these terms means splitting up the large molecules of which the heavy oils largely consist so as to give lighter and volatile substances; the second means the adding of hydrogen to the oil molecules at a high temperature, and produces similar results, though with less waste, than

"cracking". Although we have few oil wells, we have abundant supplies of a substance closely related to crude oil and in many ways resembling it chemically; this substance is coal. If coal were hydrogenated, it could be made to yield some sort of crude oil, which in its turn could be subjected to just the same refining processes as are naturally occurring oils. The process at present working most successfully is a combination of hydrogenation and "cracking", and consists of grinding coal to a fine powder, mixing it into a stiff paste with a certain amount of crude oil and forcing it, together with hydrogen, through steel cylinders, where in the presence of a catalyst consisting of the sulphides of molybdenum or tungsten, and at about 200 atmospheres pressure (3000 lb. per square inch) and a temperature of  $450^{\circ}$  C. it is transformed into a kind of crude oil. By the usual process of fractional distillation the different kinds of oil—namely, motor spirit, light oil, medium oil, and heavy oil—are separated from this mixture, and there is left a solid residue which may be used as fuel in the form of briquettes.

An advantage of some importance is that the coal used need not be of at all high quality—in fact, coals which would normally be of little value as either domestic or industrial fuel may quite satisfactorily be used for hydrogenation, so that a material of little commercial value can be successfully transformed into one of our most important and valuable raw materials.

## CHAPTER IX

### SULPHUR AND CHLORINE

SULPHUR is an element very widely distributed through nature. It is found free in the neighbourhood of volcanoes, both as crystals and as brimstone, which is impure flowers of sulphur. Combined with metals to form sulphides, it forms numerous and important metallic ores, among which may be mentioned galena or lead sulphide, blende or zinc sulphide, cinnabar or mercury sulphide, pyrites or iron sulphide, and copper pyrites—a double sulphide of copper and iron. Hydrogen sulphide, better known as sulphuretted hydrogen ( $H_2S$ ), is a gas always formed by the decay of albuminous matters, such as eggs, as is evidenced by the discoloration of metallic egg-spoons, not to speak of the odour of rotten eggs. Combined with a metal and oxygen it forms sulphates, of the general formula  $M_2SO_4$ , where M stands for metal, S for 32 parts by weight of sulphur, and O, as usual, for 16 parts of oxygen. Many natural sulphates are found, among them calcium sulphate or sulphate of lime ( $CaSO_4$ ), in the forms of gypsum, plaster of Paris and alabaster; magnesium sulphate ( $MgSO_4$ ), better known as Epsom salts; sodium sulphate or Glauber's salts; and barium sulphate ( $BaSO_4$ ) or heavy spar. Sulphur also occurs in many plants, especially in cabbages and the leguminous plants, like peas, beans, and lentils; it is found in hair, nails and horn, in sweat, and is removed from the body in urine, in the form of dissolved sulphates.

When a piece of roll sulphur is held in the hand it crackles and breaks, showing that it is a bad conductor of heat. It will not dissolve in water, even boiling nitric acid does not dissolve it, but only succeeds in oxidising some of it to sulphuric acid,  $H_2SO_4$ . It is, however, easily dissolved by one of its own compounds, carbon disulphide,  $CS_2$ , a very inflammable heavy liquid, made

by passing sulphur vapour over red-hot charcoal. Besides dissolving sulphur this liquid is an excellent solvent for phosphorus, india-rubber, and all fats and oils. It is largely used in the cycle and waterproof trades, but should be kept in stoppered bottles and handled away from a light. Carbon disulphide vapour is poisonous.

When a solution of sulphur in this liquid is allowed to evaporate slowly, sulphur crystals may be obtained similar to those found in nature. These are flat octahedra, and are quite different from the rods or prisms obtained when melted sulphur is allowed to cool. When sulphur is heated to near boiling-point and the liquid poured into cold water, it assumes a curious, stringy, elastic appearance, but such "plastic sulphur" returns to the opaque, brittle form on standing for a day or two. Sulphur, like carbon, is thus allotropic, *i.e.*, capable of existing in different forms.

When sulphur or anything containing sulphur burns in air or, better still, in oxygen, it combines with its own weight of oxygen forming sulphur dioxide ( $\text{SO}_2$ ), a suffocating acid gas, much used for bleaching and disinfecting. A rose held in the fumes is bleached, blue litmus solution poured into a bottle when some sulphur has been burned turns red, revealing the presence of an acid, sulphurous acid,  $\text{H}_2\text{SO}_3$ , which speedily passes by oxidation into sulphuric acid,  $\text{H}_2\text{SO}_4$ . Great quantities of this acid are present in the air of large towns, owing to the combustion of the sulphur in coal, and it is this acid which proves so detrimental to vegetation in manufacturing districts. When a little sulphur is heated in a test-tube it boils and passes off as sulphur vapour; this condenses upon the colder parts of the tube, forming a deposit of flowers of sulphur. It is in this way that sulphur is refined from crude brimstone.

Metallic sulphides are easily made, either by direct union of sulphur with some metal, or in the wet way by the action of sulphuretted hydrogen. Thus to form sulphide of copper, heat some sulphur in a crucible, and

when boiling add some copper filings in small quantities at a time. A black mass of copper sulphide is formed, a real chemical compound showing no traces of either sulphur or copper. If a spiral of copper wire be heated red-hot and dipped into a flask full of sulphur vapour, the copper will burn in the sulphur, forming the same black sulphide. In the same way iron filings and sulphur may be mixed together, but no chemical action occurs till the mixture is heated. The iron and sulphur are simply lying side by side; the iron may be removed by a magnet or the sulphur dissolved away by carbon disulphide. On heating, however, the two elements combine, forming a brownish-black sulphide of iron,  $\text{FeS}$ , containing only half the proportion of sulphur in iron pyrites, and therefore distinguished as ferrous sulphide.

This substance is largely made for the manufacture of sulphuretted hydrogen, a gas of daily use in all chemical laboratories. Whenever dilute sulphuric or hydrochloric acid reaches ferrous sulphide this gas is given off, and it may be used either as a gas or in the form of a saturated solution in water. By means of sulphuretted hydrogen many metallic sulphides may be made, nothing more being needed than to pass the gas through a solution of the metallic salt. Thus the presence of lead in drinking-water may be shown by allowing freshly-scraped lead to lie in water over-night, or by adding to pure water a crystal or two of sugar of lead, and then passing this gas into the liquid; in either case a brownish-black precipitate forms of lead sulphide. It is this same sulphide which is responsible for darkening oil paintings, for the white lead in the paint is converted into sulphide by this gas, which is always present where coal-gas is used. It is possible to restore the white colour by oxidising the black lead sulphide to lead sulphate, which is white, by treating the surface with an oxidising agent such as hydrogen peroxide. This is the method adopted in restoring faded paintings. Zinc white ( $\text{ZnO}$ ) is some-

times used instead of white lead, since zinc sulphide, even if made, is also white, but it has not the same covering power as white lead. To avoid a similar formation of sulphides on silver-ware, goldsmiths generally burn their coal-gas outside the windows.

Sulphur dioxide for disinfecting purposes is usually made by burning broken sulphur on some iron receptacle, such as a shovel, and in order to assist the combustion a small amount of potassium chlorate, about an ounce to every fourteen pounds, is mixed with it. The gas may

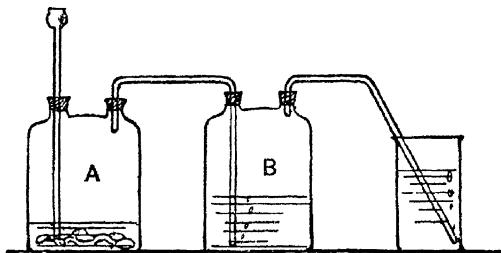


FIG. 16.—PREPARATION OF SULPHURETTED HYDROGEN.

A, Woulff bottle or flask with ferrous sulphide and dilute sulphuric acid; B, wash-bottle for solution of the gas.

also be produced by burning carbon disulphide in an ordinary kerosene lamp. All metal articles in the room should be removed, blankets and clothes hung up on poles, the whole room sprayed with water, and all outlets closed. After the combustion, four hours should be allowed for saturation by the gas, and then the windows may be opened. The chemical action here is quite different from chlorine bleaching, since the sulphur dioxide,  $\text{SO}_2$ , abstracts more oxygen from its surroundings, becoming  $\text{SO}_3$ , which in presence of water gives sulphuric acid,  $\text{H}_2\text{SO}_4$ . Sulphur bleaching is therefore a reduction process, as opposed to chlorine bleaching,

which is one of oxidation. Straw plait, blankets, silks, and animal fabrics generally are bleached by sulphur, since chlorine would destroy them; new blankets therefore always contain a fair amount of acid, which should be neutralised by adding ammonia in their first washing.

A simple method of fruit preserving, without the use of heat, depends for its action on the properties of sulphur

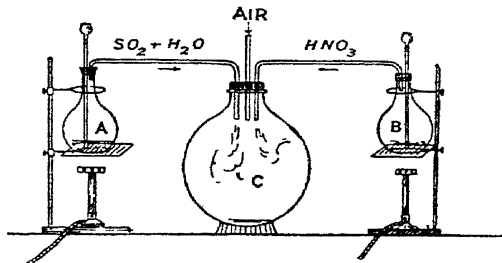


FIG. 17.—FORMATION OF SULPHURIC ACID.

A, Flask with copper turnings and sulphuric acid; B, flask with saltpetre and sulphuric acid; C, globe for mixing the gases.

dioxide in solution or sulphurous acid. The fruit is stored in sealed jars under dilute sulphurous acid or a solution of an acid sulphite (bisulphite), which has similar properties. Its preservative action is largely due to the prevention of the growth of moulds by the sulphurous acid. Before the fruit is used it must be heated to drive off the sulphur dioxide; aerial oxidation also restores the natural colour of the fruit which has been bleached out by the sulphurous acid.

The most important sulphur compound is the well-known liquid sulphuric acid,  $H_2SO_4$ , or oil of vitriol, a substance which forms the foundation of all our chemical industries. It is made by roasting sulphur or pyrites so as to produce vapours of  $SO_2$ , which are injected into



large leaden chambers supplied with steam. This would form sulphurous acid,  $\text{H}_2\text{SO}_3$ , only, and in order to supply the extra oxygen without waiting for the slow process of natural oxidation, a little saltpetre is roasted in a pot above the pyrites furnace. This supplies the necessary oxygen, not only directly, but in the shape of nitric oxide,  $\text{NO}$ , which acts as an oxygen-carrier or go-between to the fumes in the leaden chambers and the air outside, so that the process is continuous. If a little saltpetre be heated to melting in a test-tube and a pinch of sulphur dropped in, the latter burns with great vigour, owing to the increased supply of oxygen.

A more direct method of manufacture is by directly oxidising sulphur dioxide to sulphur trioxide by means of oxygen. This is known as the contact process, and is carried out with the aid of a catalyst in the form of finely-divided platinum on a support of asbestos. Great care must be taken to see that the catalyst is not "poisoned" by traces of arsenic and other impurities. The sulphur trioxide formed may be dissolved in water to form sulphuric acid, but it is actually much more soluble in sulphuric acid, with which it forms fuming sulphuric acid or  $\text{H}_2\text{S}_2\text{O}_7$ , known also as Nordhausen acid. This acid is used widely in the dyestuffs industry, and ordinary concentrated sulphuric acid may be prepared from it by cautiously diluting it with a suitable quantity of water.

The term "catalyst" is used to describe a substance which has the effect of greatly speeding up the combination of two other substances, but which does not appear to take active part in the reaction, as it remains unchanged at the end of the process. Modern chemistry abounds with examples of catalysts applied to manufacturing processes. In preparing oxygen by heating potassium chlorate (Chapter V, p. 62), the decomposition is greatly speeded up by adding manganese dioxide. This substance remains unchanged at the end of the reaction. A small piece of black, spongy platinum when held in a current of mixed coal-gas and air will glow and ignite the

mixture. This principle is made use of in some domestic gas-lighters. Other catalysts are made use of in the manufacture of ammonia, acetic acid and nitric acid, whilst in the processes of digestion numerous natural catalysts, called enzymes, play vital parts.

Pure sulphuric acid is a heavy, oily liquid, nearly double the weight of water. It has a very strong attraction for water, as may be seen by the heat produced when the acid is added to its own bulk of water. This attraction for water is further shown by the charring action which the strong acid has upon all organic sub-

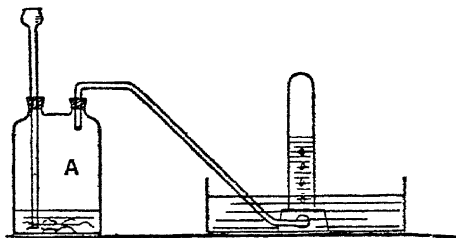


FIG. 18.—PREPARATION OF HYDROGEN.

A, Bottle with granulated zinc and dilute sulphuric acid.

stances, as when a drop falls on wood, bread, paper, or the skin. A striking experiment is one in which the acid acts upon sugar or syrup: the whole swells up into a frothy mass of spongy charcoal, distended by jets of steam.

From dilute sulphuric acid hydrogen gas may be obtained by means of zinc or iron. For this purpose a flask or two-necked bottle containing some granulated zinc is fitted with a safety-funnel and a delivery tube, and connected in the usual way with a pneumatic trough for the collection of the gas. Dilute sulphuric acid, 1 in 12, is now poured down the funnel, and hydrogen bubbles speedily appear on the surface of the zinc, as the metal

is converted into zinc sulphate. Since hydrogen and air form an explosive mixture, samples of the gas should be collected in a small test-tube and ignited; only when the gas burns quietly without any whistling noise is it safe for experimental purposes. By boiling copper in sulphuric acid the latter may be reduced to sulphur dioxide,  $\text{SO}_2$ , with formation of water and blue

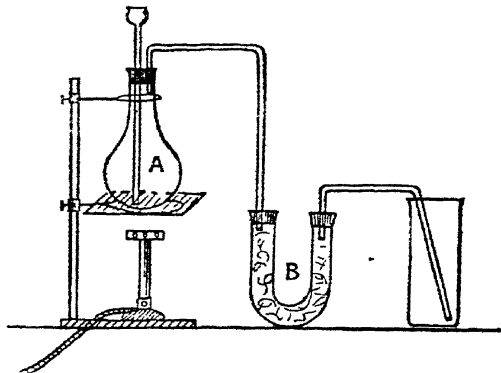
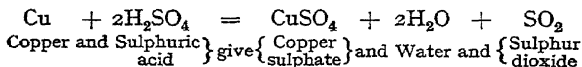


FIG. 19 — PREPARATION OF SULPHUR DIOXIDE.

A, Flask with copper turnings and sulphuric acid; B, drying-tube containing pumice soaked in strong sulphuric acid.

vitriol or sulphate of copper, and this is the process generally used in laboratories for obtaining a steady stream of  $\text{SO}_2$  gas. The following equation may be used to express this reaction :—



The necessity for heating the acid renders this method unsuitable for disinfecting. It is now possible to obtain sulphur dioxide in the form of "syphons" containing

the liquified gas under pressure. A valve on the syphon is adjusted so as to give a steady stream of gas of any rate and the liquid slowly evaporates.

By means of sulphuric acid almost all other acids may be expelled from their compounds. Thus by warming saltpetre or nitrate of potash with this acid, nitric acid or aquafortis may be obtained. If sulphuric acid be added to a little salt in a boiling tube, white, pungent

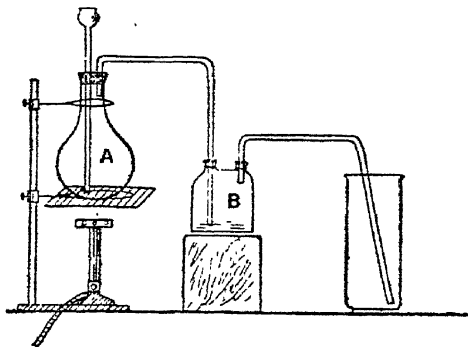
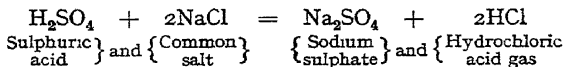


FIG. 20.—PREPARATION OF HYDROCHLORIC ACID.

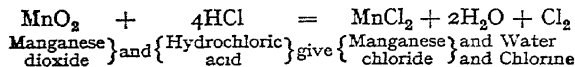
A, Flask with salt and sulphuric acid; B, small wash-bottle containing concentrated sulphuric acid.

fumes of another acid appear, and salt cake or sulphate of soda remains behind. In this case the equation would be :—



This fuming gas is hydrochloric acid, and it is made in enormous quantities in the first stage of manufacturing chlorine and bleaching-powder on the one hand, and washing-, baking-, and caustic soda on the other.

Hydrochloric acid gas is really hydrogen chloride,  $\text{HCl}$ ; it is very soluble in water, and the solution attacks most metals forming chlorides the great majority of which are soluble in water. Its chief value, however, lies in the fact that it contains  $\frac{7}{13}$  of its own weight of chlorine, which may be obtained by warming hydrochloric acid with black oxide of manganese,  $\text{MnO}_2$ , a powerful oxidising agent. The reaction may be expressed thus:—



Chlorine is a greenish-yellow gas (hence its name, from the Greek "chloros", meaning green), heavier than air, soluble in water, and possessing a characteristic suffocating odour, very trying to the throat and lungs. It is a splendid bleaching and disinfecting agent in presence of water, the oxygen of which it liberates, but it is too strong to be used with most animal fabrics, which are therefore generally bleached by sulphur dioxide. Even Turkey-red and indigo are decolorised, being converted into yellowish substitution compounds. Chlorine has a very strong affinity for all metals, many of which burn into chlorides if introduced in the state of powder or foil into chlorine gas; thin gold and platinum, which resist the strongest nitric acid, are rapidly attacked by chlorine. In using this gas as a disinfectant, it is therefore necessary to remove all metallic articles, even gilt frames.

Gold leaf and Dutch leaf, powdered antimony, zinc dust, and tin foil, may all be burned in chlorine after being slightly warmed over a bunsen flame. But the most striking experiment of this kind is the combustion of sodium. A piece of sodium the size of a pea is warmed in a spoon over a bunsen till it takes fire, and it is then lowered gently into a jar of chlorine gas; combustion still goes on, the greenish-yellow gas is consumed, and the sides of the jar are incrustated with white sodium chloride—common salt. This is a striking example of

chemical combination : out of chlorine, a poisonous gas, and sodium, an equally poisonous metal, there is formed neither gas nor metal, but a white crystalline substance which, so far from being poisonous, is actually necessary to animal life.

Chlorine water, which is simply a saturated solution of the gas, is sometimes used for bleaching, but it soon loses its power on exposure to light. Liquid chlorine—*i.e.*, chlorine gas compressed to a liquid—is on the market, and is used in enormous quantities in the chemical industry, but for domestic purposes the favourite vehicle for chlorine is the so-called “chloride of lime”, properly speaking, chlorinated lime or bleaching-powder. This is made by passing chlorine gas over slaked lime, and it parts with its chlorine on adding a very small quantity of acid. Even the carbonic acid of the atmosphere is sufficient to liberate some chlorine, but to get the full effect, a little vinegar should be added. Eau de Javelle, or chlorinated soda, is a similar bleaching-stuff, soluble in water, and much used in France. It is a mixture of sodium hypochlorite and sodium chloride; the active principle is the hypochlorite, which has the formula  $\text{NaClO}$ . It can be made by the action of chlorine on caustic soda or by electrolysis of sea-water. In bleaching-factories this process is always followed up by the use of an “antichlor”, to expel the excess of chlorine; the usual antichlor is sodium thiosulphate, known to photographers as “hypo”. Chlorates contain oxygen as well as chlorine; the best known of these is chlorate of potash,  $\text{KClO}_3$ , which parts with all its oxygen on heating, leaving potassium chloride. On this account it was formerly used for making oxygen, but it now serves as a rather more active saltpetre in explosives and fireworks.

Chlorine is the best-known member of a family of substances all found in sea-salt, and therefore called Halogens (Gr.  $\alpha\lambda\varsigma$ , salt). This group contains a liquid (bromine), and a solid (iodine), as well as the gas fluorine

—the most active chemical substance yet discovered. Taken in order, fluorine, chlorine, bromine, and iodine, they form a series descending in activity, iodine being the weakest of the set. Calcium fluoride or fluorspar ( $\text{CaF}_2$ ) is a green or purple mineral often found in lead mines and used in iron smelting as a flux. On gently warming with strong sulphuric acid, hydrofluoric acid ( $\text{HF}$ ) is obtained, a vapour much used for etching glass. Iodine was formerly obtained by burning kelp or dried seaweed, which gave ashes of carbonate and iodide of potash. It is largely used in medicine. We use iodine as an antiseptic in the form of "tincture of iodine", which is a solution of iodine and potassium iodide in spirit. Another antiseptic, called iodoform, liberates iodine slowly in contact with wounds. It is a solid, analogous with chloroform, having the formula  $\text{CHI}_3$ . Bromine finds its chief employment in photography, since the plates and many of the printing-papers are coated with a mixture of silver bromide and gelatine. Although these "halides" (halogen compounds) can be obtained in small quantities from the sea, the principal sources of world supply are the great salt deposits at Stassfurt in Germany and those in Chile, which also provide "Chile saltpetre" or sodium nitrate.

The general name "disinfectant" covers three different classes of substances: deodorants, antiseptics, and germicides. Deodorants, as their name implies, profess only to remove offensive smells, and they very often do this only by substituting another. Some of them have a feeble oxidising action, and so may be ranked as antiseptics. This section includes camphor, eucalyptus, sanitas, terebene, and other turpentine preparations, as well as nitrogen peroxide,  $\text{NO}_2$ , the heavy, brownish-red gas which is formed whenever nitric acid is added to copper or other heavy metal.

Antiseptics are, strictly speaking, substances which arrest decay, without necessarily killing the living germs themselves. Phenol or carbolic acid is a good example

of this class, since it coagulates albumen, and so paralyses the germ or destroys its feeding-ground. Sulphur dioxide has very little power over living bacteria, since these can grow even after twenty-four hours' exposure to an atmosphere containing 10 per cent. of sulphur dioxide. Boracic acid and iodoform are deservedly favourite antiseptic dressings.

For germicides—*i.e.*, germ-killers—we depend upon heat, in the shape of fire or of high-pressure steam, and upon chlorine and some of its compounds. Of these the most valuable is mercuric chloride or corrosive sublimate, 1 part of which in 5,000 parts of water is quite sufficient for complete disinfection of clothes or other substances which may be washed. It is very poisonous. Amongst other chlorine compounds which act as valuable and efficient germicides are the hypochlorites. They are easily handled, are not injurious and are non-poisonous.



## CHAPTER X

### NITROGEN AND PHOSPHORUS

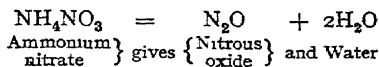
AMONG all the chemical elements there are two more intimately associated with life, and these are carbon and nitrogen. The latter element is invariably found in the living as distinguished from the formed tissues; it is an absolute necessity of life, and on this account nitrogenous foods are sometimes, though improperly, called flesh-forming. Although there is abundance of nitrogen in air—four-fifths of the total bulk of the atmosphere consisting of this gas—these supplies are not available either for animals or for the higher plants; animals require their nitrogen in organic form, as the ready-made tissues of other animals or of plants. Most plants, again, are unable to feed on atmospheric nitrogen, being dependent upon nitrogenous substances contained in soil, such as nitrates of potash and soda, ammonium salts, and others. Among the very lowest forms of vegetable life, however, there are fungi which are capable of assimilating nitrogen direct from the air and of storing it up within themselves as organic matter on which higher organisms may feed. Besides these there are nitrifying bacteria, which act upon decaying animal matter like urine or dung and by a series of oxidations convert it into nitrites and ultimately into nitrates, in which last form it may serve as plant-food. In India and South America great deposits of saltpetre or nitre are found, evidently formed by organic agency; in the former country nitrate of potash or common saltpetre; in Chile and Peru nitrate of soda usually. The process of nitrification may be seen in any dung-heap, where the potash salts are supplied by the vegetable waste and the nitrogenous matters by dung and other animals products. On the walls of stables an efflorescent, snow-like mass is often seen; this consists of wall-saltpetre or calcium nitrate, formed in a similar

way by nitrifying bacteria. From these nitrates, especially those of potash and soda, nearly all nitrogenous substances are manufactured. Another fertile source of nitrogenous material is the destructive distillation of most organic matters, as when coal is treated in gasworks. This yields ammonia compounds, as already described in Chapter VIII, but plants have no power to assimilate ammonia or its sulphate; the nitrifying bacteria in the soil must first convert these into nitrates before they are suitable for plant food.

from copper alloys, since the former metal is not affected by nitric acid, while copper at once forms a green nitrate with the usual brown fumes. Its great use, however, is for oxidising purposes. Saltpetre or nitric acid heated on charcoal till red-hot causes the charcoal to burn vigorously, as in oxygen; a few drops of nitric acid added to warm turpentine causes that liquid to burst into flame, and so on. Since nitric acid and nitrates are so rich in oxygen, as may be seen from the chemical formulæ for nitric acid,  $\text{HNO}_3$ , and saltpetre,  $\text{KNO}_3$ , they are regularly used as oxidising agents in making fireworks, gunpowder, and other explosives. Thus glycerine treated with strong nitric acid becomes nitro-glycerine, the active principle of dynamite; cotton or cellulose similarly treated forms guncotton or nitro-cellulose. Blasting gelatine is a mixture of nitro-glycerine with a little nitrated cotton or collodion, and is half as powerful again as dynamite, besides being capable of use under water. Cordite, the well-known smokeless powder adopted by the British army, is another blasting gelatine made by mixing nitro-glycerine and guncotton into a pulp with acetone and a little vaseline, and then pressing the soft pulp into threads or cords. Melinite and lyddite consist in the main of picric acid, a product of nitric acid acting upon phenol; T.N.T. (trinitrotoluene) results from the action of nitric and sulphuric acids on toluene, a hydrocarbon similar to benzene. The detonators used for the caps of cartridges and for fuses are nearly all fulminate of mercury, made by the action of nitric acid on mercury, the solution being poured into methylated spirit.

From nitric acid various oxides of nitrogen are obtained by the agency of certain metals. Thus, when nitric acid acts on copper, brownish-red fumes of nitrogen peroxide,  $\text{NO}_2$ , are given off; but if the operation be conducted in a flask, and the gas collected over water, so as to avoid contact with air, nitric oxide,  $\text{NO}$ , is formed—a colourless gas which immediately forms red fumes of the higher oxide on contact with air. More

interest attaches to nitrous oxide,  $N_2O$ , better known as "laughing-gas". It is usually made by heating ammonium nitrate and collecting the gas over warm water. The equation for this would be :—



When inhaled it produces a feeling of intoxication and short-lived unconsciousness, and on this account it is much used for dental and other slight operations. By the use of nascent hydrogen, nitric acid may be reduced to ammonia, as when saltpetre is heated in a test-tube along with caustic soda solution and a piece of aluminium. Conversely, by the action of bacteria ammonia may be oxidised, first into nitrites and then into nitrates, as in the nitre plantations of Chile.

Until relatively recently the main source of nitrates for agricultural use as fertilisers and all combined nitrogen for industrial purposes has been from either the huge natural nitre deposits in Chile or ammonia by-products from the manufacture of coal-gas. An obvious and almost inexhaustible source of nitrogen is the atmosphere, and the problem of "fixing" or combining this nitrogen in the form of compounds of use to farmers and chemists alike is one which has now found a most successful solution. It has been discovered that if hydrogen and nitrogen are passed over a catalyst, such as iron, at a high temperature and a pressure of about 100 atmospheres (1500 lb. per square inch), and rapidly cooled, some ammonia is formed. From the uncombined nitrogen and hydrogen remaining the ammonia is separated, and can be transformed into a variety of salts, the most useful of which is ammonium sulphate, well known as a fertiliser. Ammonia can also be made to yield nitric acid by passing a mixture of oxygen and ammonia over a platinum catalyst. Thus from the

atmosphere in which we live there can be obtained the necessary raw chemicals for a long series of industrial products.

Phosphorus is another element closely connected with vegetable life and also with explosives on a small scale, as seen in matches. When bones are burned in an open fire, the resulting product is bone-ash, a phosphate of lime, and when this is treated with sulphuric acid, the result is a mixture of sulphate and phosphate of lime, known in the farming world as "superphosphate". Besides bone-ash various natural phosphates are used for this purpose, such as the coprolites of Cambridge, the "land" and "river" phosphates of South Carolina, and the phosphorites of Spain and Canada. For a good many years another supply of manurial phosphorus has been obtained in the form of basic slag from steelworks; such a slag is mainly phosphate of lime, and when finely ground is worth about two-thirds of its own weight of "super-phosphate" as a fertilising agent.

Phosphorus occurs in all albuminous tissues, specially in the nervous system and in bones. Phosphatic waste is removed from the body almost entirely as phosphates in urine. Fishes are very rich in phosphorus, and when decaying give off phosphoretted hydrogen,  $\text{PH}_3$ , a gas which takes fire spontaneously. The phosphorescent glow seen on stale fish in the dark, and also in the sea at night, is of a different description, and is due to bacterial action.

Phosphorus itself is made from bone-ash and is allotropic, existing in at least two well-known forms. Common yellow phosphorus is a substance like amber, when freshly made, though it soon forms an opaque crust. It is very inflammable, and should never be handled except under water. Slight heat or friction ignites it, and it burns with great vigour, producing dense, white, poisonous fumes of phosphorus pentoxide,  $\text{P}_2\text{O}_5$ ; if allowed to oxidise without being kindled, the lower trioxide,  $\text{P}_2\text{O}_3$ , is produced.

The other form of phosphorus is a red powder, which is not readily kindled by friction or by the application of moderate heat. It is not poisonous, does not dissolve in carbon disulphide like the yellow variety, nor does it fume in air. On all these grounds it is much to be preferred to the common form in the manufacture of matches, since when yellow phosphorus is used, the workers, generally girls, suffer very severely from "phossy jaw". This is a necrosis of the bones of the face, and is caused by the corrosive action of phosphorus fumes which find entrance by some such breach as a decayed tooth.

Matches are made of wood or wax-coated thread (vestas), tipped with an explosive mixture, which can be ignited by slight friction. In common matches all the chemical action is confined to the match-head, any rough surface serving to supply the necessary friction. In the case of safety matches, which "strike only on the box", the chemicals are divided, the explosive being on the match and the phosphorus on the box. Composition for common matches contains generally five ingredients: phosphorus sulphide, as the combustible substance; potassium chlorate or nitrate, to serve as the oxidising or explosive agent; powdered glass or similar material, to promote friction; glue or other binding substance; and, lastly, colouring matter. In addition, wooden matches are generally dipped in paraffin to ensure proper combustion of the wooden stem. In safety matches the heads contain everything except the phosphorus, and in addition antimony sulphide, which produces the bluish flame and white fumes characteristic of these matches, while the rubbing surface contains red phosphorus mixed with gum and powdered glass. Fusees are composed of a mixture of charcoal and saltpetre, tipped with a striking mixture like ordinary matches, and the result is deflagration on a small scale, the charcoal burning with sparks, owing to the increased oxygen supplied by the potassium chlorate and saltpetre. Touch-paper has a similar action, since it is paper moistened with a solu-

tion of saltpetre or chlorate and then dried. In some "indoor firework" novelties sometimes found in Christmas crackers a pattern may be traced on paper with saltpetre solution, and this, when dried and touched with a red-hot match, will slowly smoulder along, tracing out the pattern as a burned line.

## CHAPTER XI

### CHEMISTRY OF THE ROCKS

THE solid earth, so far as we know it—and we know only the merest film by actual experience—is built up of rock masses more or less compact, in the form of sand and sandstone, clay, shale and slate, granite, whinstone, and other igneous rocks, not to speak of the two great classes of rocks of organic origin—namely, the carboniferous series from peat up to coal, graphite and diamond, and the calcareous rocks, limestones and chalk, from shells and corals up to marble and alabaster.

Taking clay as a sample rock, it is at once evident that there are several kinds of clay, from white kaolin or china clay and pipe clay down to the darker kinds like fuller's earth, brick clay, and blue clay, which contain in most cases a fair amount of impurities like manganese and iron. If common clay be steeped for some time in sulphuric acid it is turned into a hard, white solid—sulphate of alumina. This is soluble in water, and is now very extensively made as a clarifying agent in sewage works. If sulphate of potash be added in solution to this sulphate of alumina, and the double solution be evaporated to dryness, crystals appear of a double sulphate of alumina and potash—*i.e.*, of alum. Alum is thus a double salt, containing one acid, sulphuric, united to a pair of bases, alumina and potash. The name alum has, however, been extended to all double sulphates of members of the alumina group on the one hand, and the potassium group on the other, as under :—

Aluminium	Potassium
Chromium	Sodium
Manganese	Ammonium
Iron	

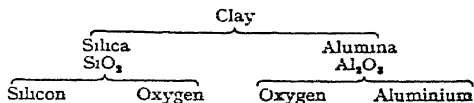
Thus soda-alum is double sulphate of aluminium and



sodium; chrome alum, much used in dyeing and tanning, is double sulphate of chromium and potassium, and so on. Alum itself is often used for clarifying and softening a hard water, in the proportion of 6 grains to the gallon, but its chief use is to act as a "mordant" in dyeing. Most animal fabrics, like silk and wool, have a fairly strong attraction, either physical or chemical, for the dyestuff employed, but in the case of cotton, linen, and most vegetable fabrics this attraction is very feeble and the colour is easily washed out. To render the colour "fast", a chemical combination must be formed between the cellulose of this fibre and the dyestuff, and this is brought about by the use of a "mordant" like alum, capable of effecting a double union, with the dyestuff on the one hand, and the fibre on the other (see p. 158).

From alum, or from sulphate of alumina, or directly from clay itself, the metal aluminium may be prepared, chiefly by electric agency, either by electrolysis or by using the intense heat of an electric arc as in the modern electric furnace. The chief commercial source of aluminium is from bauxite, hydrated aluminium oxide, frequently containing iron as an impurity. This must be removed before the aluminium can be extracted. The method of purification is to fuse the bauxite with caustic soda or sodium carbonate and extract the sodium aluminate thus formed with water. The pure oxide is precipitated from solution by means of carbon dioxide, after which it is washed, dried and ignited. From this purified aluminium oxide the metal is extracted by electrolysis. The oxide is dissolved in fused cryolite, a double fluoride of aluminium and sodium, and the heat generated by the powerful current used serves to keep the mass liquid. Carbon or silver anodes are immersed in the fused mass and the cast-iron tank acts as the cathode. The aluminium formed sinks to the bottom and is tapped off as it accumulates, whilst the alumina is added when necessary in order to keep the process continuous.

Clay is indeed, chemically, aluminium silicate, and its composition may be pictured thus :—



Alumina itself, the oxide of aluminium, is a white powder when pure, but it often occurs in nature mixed with impurities, which add considerably to its beauty and value. Corundum, or emery, is impure alumina, and among the coloured crystalline forms are included such precious stones as emerald, sapphire, ruby, topaz, oriental amethyst, and others.

Silica, the other oxide present in china clay, is the most important oxide in the earth's crust. It contains the element silicon (Si), which ranks next to oxygen in distribution, aluminium being the third element. Silica has a chemical formula  $\text{SiO}_2$ , and just as carbon dioxide,  $\text{CO}_2$ , is popularly called carbonic acid and forms carbonates, so silica is often called silicic acid, and it forms silicates, pure clay being a silicate of alumina or aluminium silicate.

Like alumina, silica occurs in nature, and that under two forms. The crystalline form of silica is familiar in quartz, or rock-crystal, which in its pure state is colourless. Many coloured quartzes have special names and rank as precious stones, thus cairngorm or smoky quartz is yellow to brown, amethyst is purple quartz. The glassy form of silica is represented by opal, and in less pure forms by onyx, chalcedony, flint, jasper, and agate.

In fact, with the exception of diamond, which is crystalline carbon, all the precious stones are either silica or alumina or some combination of these. Most of the common rocks consist of silicates, often of very complex composition, and many of these silicates find useful application. Thus mica, talc or French chalk, meer-

schaum, and asbestos are all silicates of magnesia, alumina, and iron; the felspars are mainly potash-lime and soda-lime silicates; sand and sand-stones are mainly silica itself, the colours being generally due to small quantities of iron, and so on.

Special interest attaches, however, to artificial silicates, and of these we have well-known examples in mortar, cement, concrete, and artificial stone generally, porcelain and earthenware, slag and glass. In mortar the constituents are silica, in the form of sand, plus slaked lime, and water. The resultant mixture of lime and sand hardens owing to evaporation of the water and the absorption of carbon dioxide from the atmosphere, to form calcium carbonate. When plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) is mixed with water the paste speedily hardens, apart altogether from absorption of gases or from the presence of silica, but this hard substance is soluble in water, and therefore unsuitable for use alone where water is concerned. Stucco, for example, is plaster of Paris mixed with solution of size so as to give it greater consistence and enable it to stand polishing. Hydraulic cements, made from lime containing clay, set under water, but they form insoluble compounds specially suited for standing water. Roman cement, again, is made by mixing marl or other calcareous soil with clay, so as to have one quarter of the whole consisting of clay; this really forms a silicate of lime and alumina. Portland cement is a more typical artificial silicate, and contains a calcareous mineral—*e.g.*, chalk—a siliceous mineral like sand or crushed flint, and another rich in alumina, like clay. These are mixed so as to get 75 per cent. of calcium carbonate ( $\text{CaCO}_3$ ), and the mixture is first heated to the state of "clinkers" and then ground to powder. Concrete consists of siliceous materials of all kinds—stones, pebbles, broken bricks, coarse sand, etc.—held together in a matrix of Portland cement. Slag cement is made by mixing lime with three times its weight of slag, an impure silicate of alumina and iron,

obtained from the blast-furnaces. It is nearly as strong as Portland cement, but takes longer to set.

When clay is heated to fusing-point the result is an opaque glass, as may be seen in over-burnt bricks from a blast-furnace. Common earthenware on being baked is in the porous condition known as "biscuit", and the pores require to be closed by the application of a glaze or gloss. This is always a silicate of some sort, often including borax to make it more fluid and therefore easily distributed. A handful of salt sprinkled over the earthenware in a furnace forms a surface gloss, the sodium in the salt combining with the baked clay to form an opaque glass, silicate of soda and alumina. In porcelain and china the glazing materials are thoroughly mixed with the clay, so that the result when baked is a real glass, differing from common glass only in being opaque.

When soda-ash, carbonate of soda, is heated under the foot blowpipe in a crucible of fire-clay, it melts and begins to give off the carbonic acid it contains. Small quantities of sand may now be added as long as the mixture effervesces, and on keeping up the heat for half an hour the result is silicate of soda or water-glass. This differs from glass only in the fact that it is a single silicate and dissolves in hot water, whence its name. It is often used as a preservative for coating the more porous varieties of stone. The most familiar use for water-glass, however, is in the home, where it is used in solution for preserving eggs. Its action is to seal up the innumerable pores in the shells, and so prevent the entry of bacteria.

Real glass is a complex double silicate containing silica, soda and lime; the hard glass required for combustion tubing in laboratories contains potash instead of soda, while flint glass owes its weight to litharge or lead oxide. Paste is a heavy lead glass much used a substitute for precious stones.

Heat-resisting glasses, widely used in chemical laboratories and also for making ovenware for domestic pur-

poses, are boro-silicate glasses rich in silica, and are characterised by a very low coefficient of expansion. A well-known example is Pyrex glass.

Granite may be taken as a typical fundamental or primary rock, so called because it is from such rocks as granite that other secondary rocks are derived by "weathering". As examples of secondary rocks may be mentioned sandstones, slates, shales and clays. Other igneous rocks like basalt are broken down by weathering in a similar manner.

On looking at a piece of granite it is seen to be composed of three different crystalline minerals: quartz, some felspar or other, and mica, hornblende, or similar mineral. Quartz is pure silica, the others are silicates generally of potash or soda and lime, alumina, magnesia, or iron. Under the action of weathering, granite is broken up; the quartz is washed out in the form of quartz sand; this again forms sandstones under pressure, and sandstones may in turn be changed by the presence of a volcanic or intrusive dike into quartzite and back to quartz. The silicates in granite are broken up by water into the soluble silicates of potash and soda, which are carried off to the soil and the sea by the agency of streams and rivers. The insoluble silicates of alumina and magnesia form clays of various kinds, one of which is kaolin or china-clay; again, clay under pressure becomes shale and slate, or, if greatly altered by heat and pressure, gives schists as well as the more valuable forms of mica and garnet. Many of these natural transformations are now being imitated in the laboratory, thanks to the intense heat—7,000° F.—afforded by an electric furnace, and crystalline products indistinguishable from natural forms can now be produced out of such simple materials as charcoal dust, clay, and sand. A further development is the artificial production of gem-stones such as rubies, sapphires, and emeralds of such quality as to be distinguished only with difficulty from the genuine article. Alumina, in the form of a fine powder and mixed with a

trace of the requisite accessory oxide to give the desired colour, is fed into an oxy-hydrogen blowpipe, in the flame of which it is instantly fused. It is deposited in the form of a rough-looking lump of material, the internal crystalline form of which has all the properties of the real gem-stones of natural origin. These artificial gem stones, or jewels, are valuable as hard, anti-friction bearings for the moving parts of delicate mechanisms, such as watches, electricity meters and other scientific instruments.

A large proportion of the world's ore deposits, which are of such great economic importance, are associated with igneous rocks. Weathering has revealed these ores and sometimes they have been washed out and concentrated far from their original source. This frequently results in easier working and may even have the effect of changing the composition of the ore which may make the metal more simple to extract.

It is true to say that all our metals have been derived in the first place from the igneous or primary rocks; untold quantities of many minerals still lie locked up in them. The forces of nature have liberated many of these metals in the form of ores in varying amounts and in different parts of the world. At present, there is little we can do to tap these primary supplies because they cannot be sufficiently concentrated; we must await the slow but much more efficient working of nature's processes.

## CHAPTER XII

### IRON AND OTHER METALS

OUT of the ninety elements which make up our known material world sixty-five or so are metals, but the great majority are chemical curiosities, playing little or no part hitherto in the arts and manufactures. Only some sixteen enter into the purposes of daily life, and even of these more than half are employed only to alloy with some more important metal, or else have a limited sphere of usefulness owing to cost of recovery and production. Although the term "metallic" suggests several well-known qualities, it is difficult if not impossible to give a sharp definition of a metal, and popular descriptive notions fail under close examination. Thus solidity and hardness are generally associated with a metal, yet mercury is liquid, potassium and sodium may be moulded by the fingers, and even lead may be scratched with the finger-nail; while among the non-metals there are many substances which can scratch even chilled steel. Most metals are dense, yet the lightest known solid, lithium, is a metal, and potassium and sodium also float upon water. The annexed table shows the order in which the metals appear by weight, the specific gravity indicates the weight of, say, a cubic inch of metal compared with a cubic inch of pure water at ordinary temperatures :—

#### SPECIFIC GRAVITY OF COMMON METALS.

(Water = 1.)

Platinum	.	.	21.5	Nickel	.	.	8.8
Gold	.	.	19.3	Iron	.	.	7.8
Mercury	.	.	13.6	Tin	.	.	7.3
Lead	.	.	11.3	Zinc	.	.	7.1
Silver	.	.	10.5	Antimony	.	.	6.6
Bismuth	.	.	9.8	Aluminium	.	.	2.6
Copper	.	.	9.0	Magnesium	.	.	1.75
Average			.	.	.	.	9.8

Iron is thus seen to be rather under the average for weight; a piece of iron will float in melted lead, while lead will float in mercury. The great lightness of aluminium is noteworthy: its weight is only one-third that of iron, yet its strength is hardly inferior. Most metals are malleable—that is, are capable of being beaten or rolled out into plates of greater or less thinness—and here gold heads the list, since gold may be beaten so thin as to be actually transparent, giving a thickness of less than  $\frac{1}{200000}$  inch. Silver foil has also been obtained in transparent plates. When thin gold leaf is supported on glass and looked *at*, it appears yellow as usual, but when looked *through* by holding the plate against a strong light it is green. Substances which show these differences in colour by reflected and transmitted light are called dichroic; blood and many dyestuffs and oils possess the same property. Though most of the common metals are malleable, antimony, cast-iron, and bismuth are brittle, the first especially so. Many metals are very ductile—*i.e.*, can be drawn into wire—and here again gold and silver head the list, while lead and tin, which have little tenacity, are at the bottom. Tenacity, or tensile strength, is tested by the weight required to break a wire of given dimensions, and in this respect there is a wide range from lead to steel. Taking as unity the breaking strain of lead, the metals come out in the following order:—

<i>Tenacity.</i>			<i>Malleability.</i>		<i>Ductility.</i>
Lead	.	1	Gold (highest)		Gold (highest)
Tin	.	1½	Silver		Silver
Zinc	.	2	Copper		Platinum
Gold	.	12	Tin		Iron
Silver	.	12½	Platinum		Copper
Platinum	.	15	Lead		Aluminium
Copper	.	18	Zinc		Zinc
Iron	.	27½	Iron		Tin
Steel	.	42			Lead

Metallic lustre, though characteristic enough, is not reliable as a test for metals. Certain non-metals, like



graphite and iodine, as well as many crystalline forms, possess a high degree of lustre, while many metals tarnish so readily that their lustre is only seen when a fresh cut is made on the surface scraped. Metallic ring is an even more unsafe guide, and is more a matter of hardness and elasticity than of actual metallic constitution.

All metals are fusible, though at widely different temperatures. Mercury is already melted; tin, cadmium, bismuth, and lead, the metals generally used in making solder, may be melted in small quantities even over a candle flame; zinc demands a gas flame or the red-heat of an ordinary kitchen fire; silver, copper, and gold require a cherry-red or furnace heat; cast-iron, steel, and wrought iron demand the white heat of a wind furnace; while tungsten, the most refractory of the metals, demands the intense heat of an electric arc furnace. The metals are all good conductors of heat and electricity—silver, gold, and copper being the best in these respects; and for telegraph and electric cables, and indeed in electric conductors of any kind, copper is always used, its conducting power being hardly inferior to that of silver. A rough measure of the conducting power for heat is obtained by heating in a water- or oil-bath uniform rods of different metals to which little balls have been attached by wax at stated intervals. These balls will drop off in a certain order, depending on the conductivity of the metal. To show the superiority of metals as a class in this respect, a wooden or carbon rod might be introduced into the series.

The majority of metals are attacked by chlorine, forming chlorides; most combine with sulphur to form sulphides and with oxygen to form oxides, and since most of these are insoluble in water, it is in the form of sulphides and oxides chiefly that metals are found in nature. A few metals, which have but slight affinity for the elements of air and water, are known as "noble" metals, and these often occur free or at most mechanically mixed with quartz, sand, or other impurities, from which they

are separated by purely mechanical means, like powdering and washing. These noble metals, moreover, do not readily oxidise even when melted, and this gives another means of separating them from baser metals. The metals generally ranked in this class are gold, silver, platinum, and mercury. Gold is almost always found native, either as lumps called nuggets, as gold dust, or as irregular particles embedded in a matrix of quartz. In the last case the quartz has to be crushed to liberate the gold, which is then removed by washing. Gold is fully six times as heavy as quartz, and the particles of metal fall to the bottom of the washing "cradle", while the quartz sand is carried away. From the "tailings" or quartz rubbish very minute particles of gold carried off by the stream are now recovered by the use of cyanide of potassium. This attacks gold very readily, forming a double cyanide of gold and potassium, which is removed by washing in water, and from the solution metallic gold is recovered by passing a current of electricity, as in electro-plating or by displacement with metallic zinc. The recovery of silver from lead illustrates another method of separation. If a molten mixture of silver and lead be allowed to cool, the lead is the first to crystallise out, and may be removed by skimming, thus leaving a mixture richer in silver. When the proportion of silver rises in this way to about 8 per cent., the rich mixture is subjected to a powerful hot air blast, which converts the lead into litharge or lead oxide, leaving the noble metal in the liquid state. Most metals, however, occur in the form of ores—*i.e.*, oxides, sulphides, carbonates or the like—in which the metal is in chemical combination, and frequently containing in addition mechanical impurities, such as sand and clay, often demanding elaborate processes for complete removal.

Iron occupies such a paramount place in usefulness among the metals that it demands special notice. It very rarely occurs native, except in the form of meteoric iron, those extra-terrestrial masses which fall on our

planet from time to time, and which often contain over 90 per cent. of pure iron. The metal is far too easily attacked by air, water, and other chemical agents to be found pure, and it is generally found as some form of iron ore or ironstone, from which the metal has to be extracted by laborious processes.

When scrap iron is heated smartly in air, as in a blacksmith's forge, or when a spiral of fine iron wire is burned in oxygen gas, there is formed a black oxide,  $\text{Fe}_3\text{O}_4$  (Lat. *ferrum*, iron), called magnetic oxide of iron. This is identical in composition with that natural magnet called lodestone or magnetite, found in Russia, Scandinavia, Spain, and North America, and it yields excellent iron, Swedish iron being famous for its high quality. Almost all oxides of iron are magnetic, as well as the metal itself, but this black oxide possesses this property in a more marked degree than the others.

When iron is exposed to damp air it rusts, forming a yellowish-brown oxide, which on drying forms the red powder known as rouge. Ordinary rust has the same composition as yellow and brown hæmatite, a very common iron ore; it is really iron oxide combined with water, while red hæmatite is iron oxide alone,  $\text{Fe}_2\text{O}_3$ , having the same composition as rouge. Red hæmatite occurs in the form of kidney ore, but it is often granular (pea-ore), or foliated like a schist; most ochres and umbers are soft, earthy varieties of the same ore.

Bog ironstones and the Swedish Lake ores are also forms of hæmatite, generally of the yellow or brown type, and a hard, crystalline form, similar to red hæmatite in composition, is known as specular iron ore. Most of these ores now come from Spain.

When iron is attacked by carbonic acid, carbonate of iron is formed, and this is the chemical basis of spathic ironstone as well as of the British clay ironstone and the blackband of Scotland. These two are found in layers along with coal, limestone, shale, and fireclay, and it is no uncommon thing to get out of the same shaft at once

the ironstone, coal for smelting, limestone for a flux, and fireclay for lining the furnaces. Clayband is essentially iron carbonate combined with clay, while in blackband there is bituminous or coaly matter as well, which saves fuel in the preliminary roasting.

Scattered through roofing-slate and coal, and indeed through most minerals, there are found cubes of a brassy-looking substance, called, indeed, "brassies" by miners. This is iron pyrites,  $\text{FeS}_2$ , a sulphide of iron, containing twice as much sulphur as the artificial sulphide made by combining iron and sulphur. It is hardly ever used as an ironstone, but on the other hand it is very extensively used as a sulphur supply in making sulphuric acid, since when roasted its sulphur is all burned off as sulphur dioxide.

The general principles of smelting iron and other ores, to obtain the metal, are as follows. First the ore is roasted in order to drive off sulphur, phosphorus, arsenic, water, and any other volatile products; the effect of this is to convert the whole of the metal present into oxide. The next problem is to remove the oxygen by some "reducing" agent, generally carbon in the form of coke, which combines with the oxygen forming carbon monoxide,  $\text{CO}$ , and ultimately carbon dioxide,  $\text{CO}_2$ . In order to dispose of the earthy matter associated with the ore, there is always introduced along with coke another substance called a "flux", which combines with the earthy matter to form a fluid mass called slag, which floats on the molten metal and is easily run off. Some litharge or lead oxide may be reduced on a piece of charcoal in the blowpipe flame, and little beads of lead may be obtained without any other agent. Copper oxide may also be reduced on charcoal in this way, but the reduction is more rapid when a flux is added in the shape of "fusion-mixture", the mixed carbonates of potash and soda. Under the influence of heat these carbonates swell up, and part with carbonic-acid gas,  $\text{CO}_2$ ; this under the action of the red-hot charcoal becomes carbon monoxide,

CO, just as in a common fire; finally, the monoxide abstracts oxygen from the ore again to form  $\text{CO}_2$ , thus assisting the reducing action of the charcoal. The usual flux employed on a large scale is limestone, which is carbonate of lime, and this yields carbonic-acid gas, which behaves as above. The lime, being basic, combines with acidic impurities such as silica, phosphorus and clay, to form slag. The impure iron from the blast-furnace is called pig-iron.

Pig-iron and cast-iron contain as much as 5 per cent. of carbon; nearly the whole of this may be removed by reheating in a special furnace so as to produce soft iron, generally called wrought iron, from the fact that it is rolled, hammered, etc. Steel contains up to  $1\frac{1}{2}$  per cent. of carbon.

The quantity of carbon present, though small, has a marked influence on the properties of the steel; in its turn, this governs the use to which the steel is put. The properties of greatest importance are tensile strength (resistance to stretching), hardness and toughness; there are certain other special properties, such as resistance to corrosion or the ability to retain magnetism, which may also be valuable.

The carbon is present in steel in the form of ferric carbide ( $\text{Fe}_3\text{C}$ ), which is dissolved in the iron; this compound is not an impurity, but is an essential substance without which iron would be of little practical use. Other metals, when dissolved in iron, confer on it certain special properties; many of these metals also form carbides.

The most important of these additional metals are nickel, chromium, tungsten, vanadium, manganese, molybdenum and cobalt. Steels which contain these other metals are called alloy steels. Carbon steel contains up to  $1\frac{1}{2}$  per cent. of carbon; as the quantity gradually increases, so the properties change and the use to which the steel is put varied. Steel with carbon content 0.1 per cent. is called open-hearth steel (from the

method of its production); it is used for pressings and sheet-metal work. "Machine-steel" contains 0.2 per cent. carbon and is used for making general machined parts. Structural steel, such as is used for steel-frame buildings, has 0.3 per cent. carbon, whilst a stronger and tougher structural steel has 0.4 per cent. carbon. As the carbon content rises so the hardness and toughness improve until we reach spring-steel, which contains 0.8-0.95 per cent. carbon.

When we add other metals to steel already containing some carbon, the properties can be varied still further. Steels containing nickel have improved hardness and resistance to abrasion; they are used for armour plate and ammunition, railway lines and bridge construction. They may be case-hardened, and their resistance to abrasion makes them useful for making railway lines.

Chromium-containing steels are used for armour-piercing projectiles, safes, and making castings for rock-crushing machinery. "Stainless" steels contain quite high proportions of chromium, up to 20 per cent.

As the steels become harder and tougher, so they become more difficult to cut and work. For this purpose other special steels which are still harder and tougher must be produced; these are called tool-steels and, when the cutting has to be done rapidly, they are known as high-speed tool-steels. Most high-speed steels contain one or more of the elements tungsten, chromium, vanadium, molybdenum and cobalt. Steel containing tungsten is also used for making magnets, since it has the property of strongly retaining magnetism.

Vanadium-containing steel has high tensile strength and elastic limit, so it is used for springs, gears and other stressed parts which carry heavy variable loads.

Manganese-steel, also known as Hadfield steel, after its inventor, may be either soft and ductile or very hard and tough, according to the proportion of manganese which it contains.

It is obvious that the toughest metals must be cut and

worked, and for this purpose two materials are in general use. The first and hardest substance known is the diamond. Of course, these diamonds are not gem-stones, but are less perfect stones called industrial diamonds. Not only are they expensive on account of rarity, but they are not available in large pieces. A more readily available material, which can be made in larger pieces, is tungsten carbide; it is similar to ferric carbide, and it is produced and worked with the aid of the electric furnace.

Both these materials are used in the form of shaped tips to the cutting tools. They must be carefully handled to avoid damage by chipping, since, although exceedingly hard, they are very brittle.

Metals are remarkable for the facility with which they combine with one another to form alloys. An alloy may be simply a solution of one metal in another, the particles of different metals lying side by side, as may be seen by examining a specimen under a microscope; or it may be a genuine chemical compound, differing altogether in properties from the constituent metals; or, thirdly, it may be such a compound dissolved in excess of one of the original metals. The alloys of mercury are called amalgams, and since mercury is a liquid metal, it was often used, in spite of its high price, to amalgamate gold, and so recover the precious metal from "tailings". This process has been superseded by purely chemical methods like the Pollock chlorine process and the Macarthur-Forrest cyanide process, and the only amalgam of any consequence is tin amalgam, the "silvering" used for mirrors. A new shilling rubbed in mercury is speedily amalgamated on the surface, and the mercury absorbed may be driven off by the application of heat. Copper amalgam is used in dentistry, for stopping teeth.

The commonest alloys are those of copper, zinc, tin, and lead. Copper and zinc form brass, copper and tin form bronze, while lead is the basis of pewter and of the different sorts of solder. Standard gold, formerly used in coinage, is 22-carat gold—*i.e.*, it contains 22 parts of

gold out of a total of 24, the rest being copper. Standard silver contains 37 parts of silver to 3 of copper, and the alloy now used for pennies and other so-called "coppers" is really a bronze consisting of 97 per cent. of copper, 0.5 of tin, and 2.5 of zinc. Of recent years many new bronzes have been introduced, especially in shipbuilding, such as manganese bronze, phosphor bronze, silicon bronze, and the like, all of which contain copper and tin, with the addition of a small quantity of the name substance. Since the names of many of these alloys are often conventional, and in some cases misleading, the bird's-eye view of the composition of common alloys will be found useful (see table).

COMPOSITION OF ALLOYS.

Alloy.	Copper. Cu.	Zinc. Zn	Tin. Sn.	Lead. Pb.	Bismuth. Bi	Antimony. Sb.	Aluminium. Al.	Nickel. Ni.	Iron. Fe.
Brass . . .	*	*							
Bronze . . .	*		*						
Bell- and Gun-metal . .	*	*	*						
Phosphor Bronze.	*		*	and	Phosphorus				
Silicon Bronze .	*		*	and	Silicon				
Manganese Bronze	*		*	and	Manganese				
Delta Metal . .	*	*							*
German Silver .	*	*						*	
Aluminium Gold .	*						*		
Solder . . .			*	*					
Quick Solder .			*	*	*				
Pewter . . .			*	*					
Type-Metal. .			*	*		*			
Britannia } or {	*	*	*	*		*			
Metal } or {	*		*	*		*			
Fusible Metal .			*	*	*				

The influence of impurities on physical properties is particularly noticeable in the metal copper. Where used



for electrical purposes, copper must be exceptionally pure, otherwise its resistance to the passage of current will be too great to be of practical use. In order to obtain it in its highest state of purity, the metal is first extracted from its ore and then purified electrically in a manner similar to electroplating. The crude lump of copper forms one electrode of the cell, and a thin sheet of pure copper acts as the other; a solution of copper sulphate separates them. When the electric current passes from the lump of crude copper to the copper sheet, only pure copper is deposited on the sheet, and the impurities fall to the bottom of the vat in which the electrolysis takes place. Alloying about 0.9 per cent. cadmium with pure copper greatly increases the tensile strength of wire, without materially lowering conductivity.

We have already mentioned the use of nickel for producing alloy steels; it is also used in large quantities for nickel-plating. The ore from which it is extracted contains copper as well as nickel, and the two are difficult to separate. Use is made of a rather unexpected property of the element nickel. The roasted ore is treated with water-gas, a mixture of carbon monoxide and hydrogen, which reduces the oxides to metal. Carbon monoxide alone is then passed over the mixture of metals heated to  $80^{\circ}\text{C}$ . A volatile compound is formed, called nickel carbonyl  $\text{Ni}(\text{CO})_4$ , and this is led over pellets of pure nickel at a higher temperature (about  $180^{\circ}\text{C}$ .), at which it decomposes; the pure metallic nickel is deposited on the nickel pellets and the carbon monoxide set free for further use. It is interesting to note, in passing, that iron and cobalt also form volatile carbonyls; these three metals possess many other properties in common. If the mixed nickel-copper ore is smelted direct, the alloy so formed is known as Monel-metal and contains about 2 parts nickel to 1 part copper.

The construction of all-metal aircraft demands a material which combines maximum strength with

minimum weight. The obvious choice, from the point of view of lightness, is aluminium or magnesium, but both these are soft and easily corrode.

Special alloys have been produced which, for their weight, have extraordinary strength, lightness and resistance to corrosion. For example, Duralumin contains, in addition to aluminium, small quantities of copper, magnesium and manganese. Magnalium is aluminium alloyed with about 10 per cent. of magnesium. On the other hand, Electron and DOWMETAL are mostly magnesium with aluminium, copper and zinc added.

Hydrochloric acid attacks most metals, forming chlorides, all but a few of which are soluble in water. The acid generally used for etching or dissolving metals is *aqua fortis* or nitric acid, which forms a nitrate of the metal, evolving at the same time heavy red fumes of nitrogen peroxide,  $\text{NO}_2$ , a rather useful disinfectant. Gold and platinum are not affected by either of these acids, but succumb to a mixture of them, forming chlorides. This may be shown by treating gold leaf with strong nitric and hydrochloric acid in separate test-tubes; no action occurs, but, on mixing the contents, nitrohydrochloric acid or *aqua regia* is formed, and this evolves chlorine gas, converting the metal into chloride. The chloride of gold, at one time used in photography for "toning", is prepared in this way.

Cold sulphuric acid acts but feebly upon most metals except zinc and iron; with these it forms sulphates, liberating hydrogen gas, and for laboratory purposes hydrogen is generally made by means of zinc and sulphuric acid, as described on p. 103.

Such action, indeed, furnishes the best definition which can be given of a metal as a substance capable of replacing the hydrogen of an acid so as to form a "salt". It is scarcely correct, therefore, to speak of nitric acid as "dissolving" a metal; what it does is to form a soluble nitrate of the metal, and, on evaporating such a solution to dryness, the metal is not recovered as such, but only

the crystals of nitrate. If hot sulphuric acid be employed, as in attacking copper, the acid itself is reduced as well as decomposed, and the gas coming off is not hydrogen but sulphur dioxide,  $\text{SO}_2$ , formed from the sulphuric acid,  $\text{H}_2\text{SO}_4$ . Nitric acid never yields hydrogen but various oxides of nitrogen, generally the brownish-red fumes of the peroxide,  $\text{NO}_2$ . Any hydrogen which might be formed is immediately oxidised to water by the excess of nitric acid.

Many metals can unite with oxygen and similar elements in several proportions; thus lead (symbol Pb, *plumbum*) has got litharge,  $\text{PbO}$ , a puce-coloured dioxide,  $\text{PbO}_2$ , and minium or red lead,  $\text{Pb}_3\text{O}_4$ . All these compounds illustrate the law of multiple proportions under the Atomic Theory; the proportion of oxygen is always found to run in multiples of 16, and lead in multiples of 207—in other words, of the atomic weights of these elements.

Many metallic salts are used in the arts, generally as pigments. When lead is combined with vinegar, sugar of lead or lead acetate is formed, and from a solution of this almost any lead salt may be made. Thus chrome yellow or lead chromate is formed by adding chromate of potash to sugar of lead solution; white lead or carbonate of lead by adding carbonate of soda or ammonia, while the blackening effect of sulphur gases on paint may be shown by adding a few drops of sulphuretted hydrogen in solution to the same liquid so as to form sulphide of lead, similar in composition to galena, the common lead ore. Mercury has two chlorides: the lower chloride ( $\text{HgCl}$ ) calomel and the mercuric chloride ( $\text{HgCl}_2$ ) or perchloride, corrosive sublimate. Vermilion is mercuric sulphide, and has the same composition as cinnabar—a natural ore. Silver is remarkable for the way in which many of its salts are altered by light, in this way laying the basis of photography (Chapter XVIII). When silver is attacked by nitric acid, the salt produced is silver nitrate or lunar caustic, used in medicine.

When sulphuric acid acts on copper turnings, sulphate of copper or blue vitriol is formed; green vitriol or copperas is the sulphate formed when iron is the metal attacked; pink vitriol and white vitriol are sulphates of manganese and zinc, respectively. Zinc white, used by painters as a substitute for white lead, is zinc oxide, whereas white lead is a carbonate. Carbonate of soda is soda-ash, or, in the crystalline state, washing soda or soda crystals; baking-soda is bicarbonate of soda. Pearl-ash is carbonate of potash; smelling salts are carbonate of ammonia, and so on.

Some of these metallic salts are soluble in water, others are insoluble in water but soluble in some other reagent, and in this way it is possible to draw up a scheme of analysis suitable for detecting and separating the ingredients of a complex mixture of salts. For the details of these methods students must consult some work on chemical analysis.

## CHAPTER XIII

### CARBON AND ITS COMPOUNDS

UP to the present, the bulk of our discussions have centred around the behaviour and composition of inanimate or mineral matter, the study of which is often called inorganic chemistry. A large field remains, however, which is concerned with the chemistry of substances associated, closely or otherwise, with living matter. Such chemical substances usually contain the element carbon in combination with such other elements as hydrogen, oxygen, nitrogen or perhaps sulphur.

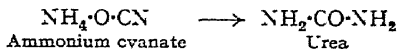
On account of this intimate association with living matter they have become known as organic compounds, and their study is frequently called organic chemistry. A better and more general term, however, is the chemistry of the carbon compounds.

As is often the case, where a dividing line is drawn, an example quickly turns up which cannot be satisfactorily accommodated on either side of the line. Such a substance is urea, the characteristic waste product excreted in the urine of mammals, and therefore intimately associated with living matter.

It is only about 120 years ago that all these organic compounds, of which urea is a typical example, were considered to require, for their formation, the intervention of a "vital force", in some way inherent in living matter.

The story, unfortunately somewhat discredited by recent research, is told that the chemist Wöhler attempted to prepare crystals of the inorganic salt ammonium cyanate by evaporating a solution of this substance. Instead, he obtained crystals of urea, an organic substance, well known for fifty years previously as the main constituent of urine, but produced on this occasion from inorganic sources and without the "vital force".

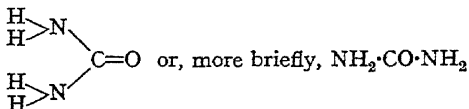
The two substances contain the same proportions of carbon, hydrogen, oxygen and nitrogen (equivalent to  $\text{CH}_4\text{ON}_2$ ), so the change is one of internal rearrangement of the atoms comprising the molecule, thus :—



The fact that more than one chemical substance has the same empirical formula (that is, the same quantitative composition) but different chemical and physical properties is frequently encountered amongst carbon compounds. The effect is called "isomerism", and it is due to the atoms of which the substance is built being arranged or linked up in a different manner.

When dealing with inorganic substances it is generally sufficient to express their molecular formulæ in the usual manner, without bothering to show how the constituent atoms are linked up to form the molecule. For instance, the formula  $\text{H}_2\text{SO}_4$  means only sulphuric acid and nothing else.

The possibility of isomerism in carbon compounds makes it necessary to draw some sort of picture of the molecule of the substance under discussion. Such pictorial representations are called structural formulæ and play a large part in the theory of organic chemistry. Thus urea, already mentioned, has a molecular formula  $\text{CH}_4\text{ON}_2$ , but its molecule is more accurately represented when written :—



It will be noticed that the atoms are linked by lines (or dots), called bonds, and each atom has as many bonds associated with it as correspond to its valency (see p. 24).

Thus, hydrogen has one bond, oxygen two, nitrogen three or sometimes five and carbon four.

In addition to the compounds which carbon forms with other elements, such as those already mentioned, it also possesses the most unusual and outstanding property of combining with itself. Thus, all the carbon compounds with which we deal consist of carbon atoms in either straight or branched chains or, alternatively, in closed ring-like systems. The number of carbon atoms in this assemblage or nucleus, together with its shape and size, has a most important bearing on the properties and behaviour of the compounds into which it enters.

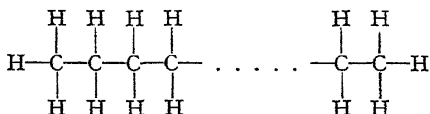
During the discussion on ammonia (p. 30) it was pointed out that, in certain respects, the salts of ammonia—for example, ammonium chloride  $\text{NH}_4\text{Cl}$ —had properties resembling those of metallic salts. The  $\text{NH}_4$ -group (ammonium) could thus be regarded as a hypothetical metal. Such “compound elements” are called radicals. Another radical, this time one behaving in the manner of an acid, is the cyanide ( $\text{CN}-$ ) group in, say, potassium cyanide,  $\text{KCN}$ . In its behaviour it is analogous to the halogens.

It will be noticed, as we progress in the study of the chemistry of the carbon compounds, that we have a number of radicals or groups which confer certain characteristic properties on the compounds into which they are embodied. This is a feature of organic chemistry which has no real parallel with inorganic chemistry, but which, when accepted and understood, rationalises and considerably simplifies the study of the subject.

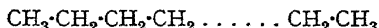
In our examination of the distillation products of coal we observed that, amongst other things, a number of compounds of carbon and hydrogen were produced. The simplest of these is a gas called methane, with the formula  $\text{CH}_4$ .

Of those elements which form compounds with hydrogen at all, few form more than two; carbon, on the other hand, is known to form more than

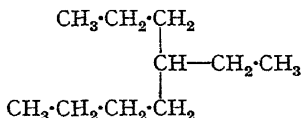
2,000. These compounds of carbon and hydrogen are called hydrocarbons; methane is the simplest of a series which are given the general name of the "paraffins". Numbers of the paraffin series are found in mineral oils, of which the familiar "paraffin-oil" is one, and they have the general formula of  $C_nH_{2n+2}$ , where  $n$  is any number from 1 upwards. The paraffins are built up from long chains of carbon atoms to which hydrogen atoms are attached thus :—



This is more conveniently written :—



Instead of being straight, the carbon chains may be branched in a number of ways, for instance :



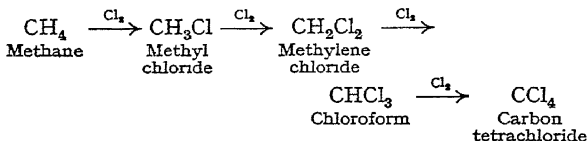
The paraffins do not react at all easily with other substances; it is to this lack of chemical affinity that their name is due. When burned in air, carbon dioxide and water are formed. The only other reaction they undergo is in conjunction with the halogens, particularly chlorine.

Methane is found in coal-mines, where it is known as fire-damp, and in marshy localities, where it gets the name of marsh gas. As stated, it is present in coal-gas, wood-gas (obtained in the destructive distillation of wood) and in natural gas, which is derived from petroleum deposits. It forms explosive mixtures with air and, if



in such a mixture there is insufficient oxygen for complete combustion, the resulting products after explosion include some carbon monoxide. It is this poisonous carbon monoxide which is the danger in the "after-damp" left after a mine explosion.

Methane combines with chlorine in such a way that the hydrogen in the molecule is replaced in stages by chlorine to form substitution products, thus :—



At least three of these compounds are of everyday importance. Chloroform ( $\text{CHCl}_3$ ) is well known as an anæsthetic; carbon tetrachloride ( $\text{CCl}_4$ ) is used in fire extinguishers under the name of "Pyrene" and is also of use in dry-cleaning owing to its properties as a solvent for grease; methyl chloride ( $\text{CH}_3\text{Cl}$ ) is sometimes used in refrigerating machines in the same way as is ammonia or carbon dioxide.

If the members of the paraffin series are arranged in order of the number of carbon atoms they contain, they are found to graduate slowly but regularly from gases ( $\text{C}_1$  to  $\text{C}_4$ ), through liquids ( $\text{C}_5$  to  $\text{C}_{15}$ ), to wax-like solids ( $\text{C}_{16}$  and over). Such a series is called a homologous series.

Amongst the constituents of coal gas is one containing proportionately less hydrogen than methane, having the formula  $\text{C}_2\text{H}_4$ ; it is called ethylene. Chemically, it is much more reactive than methane, and readily combines with halogens. It also takes up hydrochloric acid gas and forms ethyl chloride ( $\text{C}_2\text{H}_5\text{Cl}$ ). Its structure is expressed by the formula  $\text{CH}_2\text{:CH}_2$ , and it will be seen to contain a "double bond", which indicates that it is "unsaturated". Indication of this state of unsaturation by the use of a double bond represents a weaker than normal

link between the two carbon atoms. As we have seen, the normal single bond is a strong link because the paraffins are chemically inert. Conversely, the activity of the doubly bonded carbon atoms shows that the union is weak and capable of taking up other elements in order to revert to the stronger, single-bonded state. The gas acetylene,  $C_2H_2$ , contains a triple bond ( $CH\equiv CH$ ) and is even more reactive.

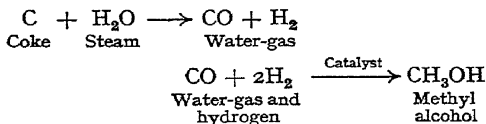
We have already made reference to methyl chloride ( $CH_3Cl$ ) and ethyl chloride ( $C_2H_5Cl$ ). The names methyl and ethyl represent the radicals,  $CH_3-$  and  $C_2H_5-$  which also form part of a homologous series of which the following are the first six "alkyl radicals":—

methyl, $CH_3-$	butyl, $C_4H_9-$
ethyl, $C_2H_5-$	amyl, $C_5H_{11}-$
propyl, $C_3H_7-$	hexyl, $C_6H_{13}-$

The group  $-CH_2-$ , which represents the common difference between neighbouring radicals, is called the methylene group.

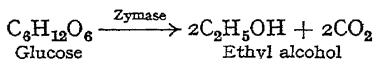
Various characteristic groups can be attached to any of these radicals, in place of the halogens mentioned. Thus, if the group  $OH-$  is used to replace  $Cl-$ , we have substances known as alcohols. For instance  $CH_3OH$  is methyl alcohol, a product of the destructive distillation of wood, called wood spirit.  $C_2H_5OH$  is ethyl alcohol, or spirit of wine, is the active principle of all intoxicating beverages. Propyl alcohol,  $C_3H_7OH$ , is contained in fusel oil, as is also amyl alcohol,  $C_5H_{11}OH$ .

Methyl alcohol can be produced synthetically by passing a compressed mixture of water-gas and hydrogen over a heated catalyst consisting of zinc oxide and chromium oxide.



It is used as a solvent in the preparation of lacquers and varnishes; in the organic chemical industry it is used, directly or indirectly, in the manufacture of many fine chemicals, such as drugs, dyes and photographic chemicals.

Ethyl alcohol, also called spirit of wine, is obtained by both synthetic methods and fermentation processes. The simplest method is the fermentation of sugars, such as glucose, by means of yeast, as in the brewing of beer, making wine and spirits. Yeast, in common with several other fungi, is able to secrete minute quantities of a catalyst which causes the breakdown of a complex compound like sugar into the simpler substances alcohol and carbon dioxide. These catalysts, of which there are many, and which encourage certain specific reactions, are called enzymes. The enzyme which converts glucose into alcohol is called zymase.



Glucose, suitable for this fermentation reaction, can be readily produced, in quantity, by treating starch with hot dilute acid. The starch may be in the form of potatoes or grain; molasses or even sawdust and waste wood can, by suitable treatment, be used as raw materials.

The alcohol produced by fermentation is dilute and mixed with other substances, such as the raw materials from which it is formed. It is concentrated by distillation. The distillate is called rectified spirit, and contains up to 95 per cent. of ethyl alcohol. Pure alcohol is called absolute alcohol; it has the property of strongly absorbing water.

The industrial uses of alcohol are as a source of fuel and power, as a solvent and, in chemical manufacture, as a starting product for certain medicinal chemicals.

The most familiar form in which alcohol is used, either domestically or industrially, is as methylated spirit or

industrial spirit. Methylated spirit is alcohol rendered unfit for human consumption by the addition of crude wood spirit (methyl alcohol), pyridine (providing its characteristic smell), a small quantity of mineral oil and a trace of a violet dye.

Industrial spirit, which is used for purposes for which methylated spirit is not suited, contains 5 per cent. of crude wood spirit only. When mixed with water,

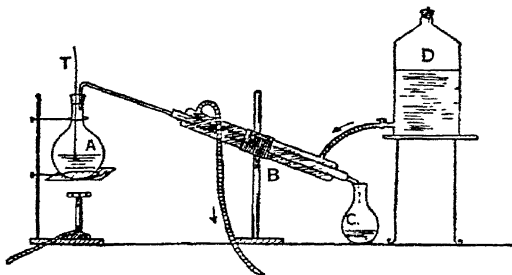
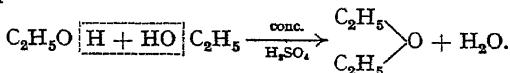


FIG. 22.—FRACTIONAL DISTILLATION.

A, Distilling flask with thermometer (T); B, Liebig's condenser; C, receiving flask for distillate, D, water supply.

methylated spirit turns cloudy, whilst industrial spirit remains clear.

If alcohol is heated with concentrated sulphuric acid, we obtain a substance called ether. The reaction is really one of removing the elements of water from two molecules of alcohol; the ether formed from ethyl alcohol is diethyl ether,  $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ . It may be expressed :—



If the mixture is heated rather more strongly, the alcohol decomposes, and we get the gas ethylene instead.

Ether is well known as an anæsthetic. If methylated spirit is used instead of alcohol, we get methylated ether, which is less pure, being mixed with dimethyl ether.

Other members of the ether family can be produced by subjecting the corresponding alcohols to the same treatment; diethyl ether is the most widely used. It finds application on a very large scale as a solvent in the preparation of collodion, Chardonnet silk and certain explosives.

It is of interest to note that some of the constituents of certain essential oils are ethers; for example, anethole and eugenol, which are the chief components of oils of anise and clove respectively, are complex ethers containing the methoxy-group  $\text{CH}_3\cdot\text{O}-$ .

If alcohol is oxidised, by means of chromic acid, we obtain an aldehyde; the name is derived from *dehydro*-generated *alcohol*. Methyl alcohol yields the gas formaldehyde,  $\text{H}\cdot\text{CHO}$ , which, when dissolved in water, is known as formalin. The oxidation of ethyl alcohol gives acetaldehyde,  $\text{CH}_3\cdot\text{CHO}$ .

Aldehydes are very reactive, and have many uses in synthetic organic chemistry. They are active reducing agents and will reduce ammoniacal silver nitrate to produce a silver mirror. This provides a means of silvering glass by chemical means.

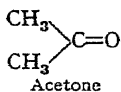
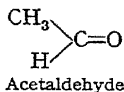
An important derivative of acetaldehyde is chloral, which is obtained by treating warm rectified spirit with chlorine. The product,  $\text{CCl}_3\cdot\text{CHO}$ , combines with water to form chloral hydrate, well known as the main constituent of some sleeping-draughts.

Some of the higher aldehydes are constituents of essential oils, and are used in perfumery; others are flavouring essences. Amongst these, citral and citronellal are found in oil of lemon; benzaldehyde and cinnamic aldehyde in oil of bitter almonds and cinnamon respectively; **vanillin** is an aldehyde. Many sugars are also aldehydes.

Another chemically similar substance is obtained

from the destructive distillation of wood; it is found to have the formula  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ , and is called acetone.

Acetone is a ketone, and behaves chemically in many ways similarly to acetaldehyde. It will be seen to be structurally related to acetaldehyde if the two formulae are compared :—



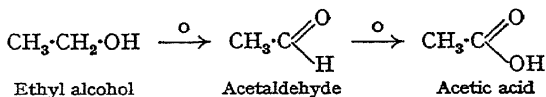
In general, the ketones behave similarly to aldehydes; the characteristic aldehyde group is  $-\text{CH}\cdot\text{O}$ , and that of a ketone  $=\text{C}\cdot\text{O}$ .

Acetone finds many uses as a solvent, particularly in the preparation of varnishes, cordite (smokeless powders) and celluloid. Acetylene is stored in cylinders packed with porous material soaked with acetone, in which acetylene is very soluble. It is also the starting point for the manufacture of chloroform and iodoform.

Many perfumes and essential oils are complex ketones; for example, musk has muscone for its active principle. It would appear that there is some connection between odour and molecular structure, since so many perfumes are either aldehydes or ketones. Many of the sugars are also ketones; of these, fructose is the best known.

By carrying further the oxidation of alcohol, beyond the stage of an aldehyde, we obtain a fatty acid, characterised by the group  $-\text{CO}\cdot\text{OH}$ .

The stages of this reaction may be expressed :—



Methyl alcohol passes through the stages of formaldehyde to formic acid; ethyl alcohol yields first acetaldehyde, and finally acetic acid.

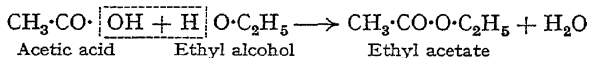
Acetic acid is familiar to us in everyday life under the name of vinegar. The best vinegar is produced by allowing the fermentation of beer to proceed to completion, the ethyl alcohol being converted into acetic acid. It is also obtained as one of the products of the destructive distillation of wood, and it is the acetic acid which contributes to the mainly acid reaction of "pyro-ligneous acid", as the distillate is called. Its main constituents also include methyl alcohol and acetone, as well as acetic acid. When pure, acetic acid readily solidifies, in which form it is called glacial acetic acid.

Its uses include those of solvent, and also a reagent in the preparation of artificial silk and "non-flam" cine-film.

The name fatty acid is due to the fact that these acids are intimately concerned in the formation of the natural fats (see p. 179).

We have seen that the alcohols are typified by the OH- group, so, by analogy with inorganic chemistry, some reaction might be expected between an alcohol and a fatty acid. The product of such a reaction is called an ester, and is the counterpart of a salt, in inorganic chemistry, formed by the action between an acid and a base.

Acetic acid and ethyl alcohol react, in the presence of sulphuric acid, to form the ester ethyl acetate :—



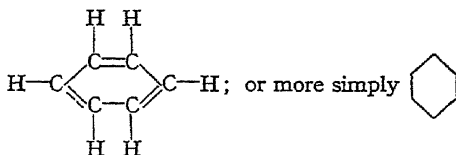
Many esters are fragrant liquids and are used as artificial flavouring essences or perfumes. Ethyl formate is used to give a flavouring of rum; amyl acetate has a pronounced smell of "pear drops"; other esters have flavours or characteristic smells of pineapple or apple.

An important group of compounds called amines are derived, in theory, by substituting one or more of the hydrogen atoms of ammonia by alkyl radicals. Thus :

$\text{CH}_3\cdot\text{NH}_2$  is methylamine,  $(\text{CH}_3)_2\cdot\text{NH}$  is dimethylamine and  $(\text{CH}_3)_3\cdot\text{N}$  is trimethylamine. These are examples of primary, secondary and tertiary amines, respectively.

The amines are important in the study of the chemistry of animal and plant products (called biochemistry), as we shall see later; they also are used in the preparation of dyestuffs, drugs and other fine chemicals.

Numerous chemical raw materials are obtained in the destructive distillation of coal; amongst them is a liquid hydrocarbon having the formula  $\text{C}_6\text{H}_6$ , and named benzene (p. 92). Benzene is rather special, in that it consists of a chain of six carbon atoms linked together in the form of a ring, with a hydrogen atom attached to each, thus :—



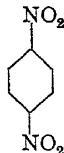
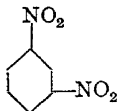
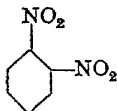
Compounds of benzene and other closed-chain hydrocarbons are called aromatic compounds, in distinction to the open-chain compounds, which are called aliphatic. Most of the chemistry of natural products is concerned with aliphatic compounds, but the wide field of synthetic chemical products, such as dyestuffs, drugs, plastics and explosives, are entirely dependent on the aromatic compounds, of which benzene is one of a series.

Benzene itself is useful as a solvent of such substances as fats and rubber and many organic compounds. Its compounds, however, are even more important than the hydrocarbon benzene. In contrast to aliphatic hydrocarbons, it is acted upon by concentrated sulphuric acid to form a substituted compound, called benzene sulphonic acid,  $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ . When treated with a mixture of concentrated nitric and sulphuric



acids, an oily liquid is formed, which is nitrobenzene,  $C_6H_5 \cdot NO_2$ . It is possible to carry this nitration further, and to produce di-nitrobenzene,  $NO_2 \cdot C_6H_4 \cdot NO_2$ , which is a solid. Nitrobenzene has a strong smell of bitter almonds, is poisonous, and is used as a scent for cheap soap under the name of "oil of mirbane". In a manner somewhat similar to the paraffins, benzene can be halogenated.

When two of the hydrogen atoms are substituted, as for instance in di-nitrobenzene, the replacement can take place in one of three positions in the benzene ring to yield three compounds with the same formula but having differing physical properties (e.g. melting points):—



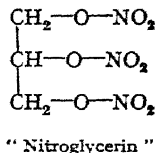
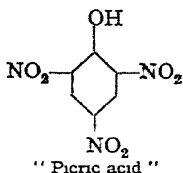
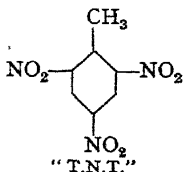
"ortho-" (*o*-),  $116^\circ$     "meta-" (*m*-),  $90^\circ$     "para-" (*p*-),  $172^\circ$

These compounds are all isomeric (see p. 139), and, in order to distinguish them, they are given the names of *ortho*-, *meta*- or *para*-dinitrobenzene, to indicate that the second substituted group is either adjacent to, next-but-one to, or directly opposite to the first group in the benzene ring.

If one of the hydrogen atoms is replaced by  $OH^-$ , we get phenol or carbolic acid,  $C_6H_5 \cdot OH$ , a substance obtained principally from coal-tar, and most important in the production of synthetic materials like explosives and plastics, as well as being an excellent antiseptic.

When the substituent of one of the hydrogen atoms is the methyl group,  $CH_3^-$ , we obtain toluene,  $C_6H_5 \cdot CH_3$ , also derived, along with xylene and benzene, from the distillation of tar products. By nitrating toluene—that is, treating it with a mixture of concentrated nitric and sulphuric acids under carefully controlled conditions—

we obtain tri-nitrotoluene, well known as the high explosive "T.N.T." If phenol is similarly nitrated, the product is tri-nitrophenol or picric acid, another high explosive.



Glycerin, when similarly treated, forms glycerol tri-nitrate; this is not chemically a nitro-body, like picric acid, but a tri-nitrate, although commonly called nitroglycerin.

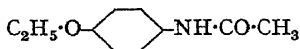
Whilst on the subject of explosives, it is of interest to note that "Amatol" consists of T.N.T. 1 part and ammonium nitrate 4 parts. "Dynamite" is made by absorbing 3 parts nitroglycerin in 1 part of a porous earth called kieselguhr. "Carbodynamite" is a variant of this, in which the nitroglycerin is absorbed on to cork-charcoal or sawdust. "Blasting gelatine" consists of a mixture of collodion-cotton (also called nitrocotton, on p. 162) and nitroglycerin; "Gelignite" consists of nitroglycerin, collodion cotton, potassium nitrate and wood flour. "Gun-cotton" is made by gelatinising cellulose nitrate (also called collodion cotton or nitrocotton) with acetone or ethyl acetate. "Cordite" is a mixture of 52 per cent. gun-cotton, 42 per cent. nitroglycerin and 6 per cent. vaseline. Another high explosive, for blasting purposes, produced in U.S.A., is nitrostarch; it is similar to gun-cotton.

If the aldehyde group  $-\text{CHO}$  is introduced into the benzene nucleus, we get benzaldehyde,  $\text{C}_6\text{H}_5\cdot\text{CHO}$ , which is oil of bitter almonds. Bitter almonds contain a glucoside (which is a compound containing the sugar glucose) called amygdalin, together with the enzyme

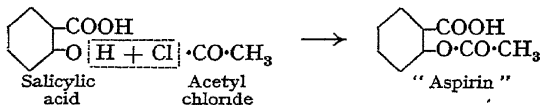
emulsin. When the almonds are crushed, the enzyme acts upon the glucoside and hydrolyses it, giving benzaldehyde, glucose and prussic acid. Its name, oil of bitter almonds, thus explains its origin; benzaldehyde thus produced may be dangerous to use as a flavouring essence unless carefully purified.

The introduction of the characteristic acid group—COOH gives benzoic acid,  $C_6H_5 \cdot COOH$ , first obtained by subliming the resin called gum benzoïn, whence the name benzene is derived.

A most important substance, aniline, is obtained from coal-tar; it is an amine with the formula  $C_6H_5 \cdot NH_2$ , and is the starting-point for numerous dyestuffs, often called aniline dyes. If aniline is heated with glacial acetic acid, a substance called acetanilide is formed, also known under the name "antifebrin". Its formula is  $C_6H_5 \cdot NH \cdot CO \cdot CH_3$ , and it is a constituent of some cold-curing preparations and certain headache cures. A disadvantage of its use is that, in the stomach, it tends to be hydrolysed back to aniline and acetic acid. As aniline is poisonous, these fever-cures may be dangerous. The danger is removed if an ethoxy-derivative of acetanilide is used instead; this substance is called "phenacetin":—



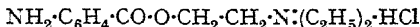
Another much-improved pain-reliever is "Aspirin", which is derived from salicylic acid,  $OH \cdot C_6H_4 \cdot COOH$ . Oil of wintergreen consists mainly of methyl salicylate, the methyl ester of salicylic acid. If salicylic acid, which is *o*-hydroxy benzoic acid, is acetylated by treatment with acetyl chloride, the result is aspirin or acetyl salicylic acid:—



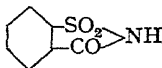
As already mentioned, numerous drugs, antiseptics and other synthetic chemical products are prepared from benzene or its derivatives.

A most useful antiseptic of the hypochlorite type is chloramine-T, which is a by-product in saccharin manufacture; it is non-toxic and non-corrosive. Derived from toluene, its chemical name is sodium *p*-toluene sulphonechloramide,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{N}\cdot\text{ClNa}$ .

Of the synthetic drugs, one of the simplest is Novocaine, which is used nowadays instead of cocaine as a local anæsthetic in dentistry. We have already observed, in the aldehydes and ketones, some connection between chemical constitution and smell; a similar, though much more complex relationship is traceable between chemical constitution and physiological action. Certain drugs, such as cocaine, possess a basic structure which, by suitable modification, can be endowed with all the desired beneficial properties and divested of the dangerous ones. Novocaine, which can be synthesised from *p*-aminobenzoic acid, ethylene chlorohydrin and diethylamine, has the structure



A somewhat unexpected derivative of coal-tar products is saccharin, the name of which is *o*-benzoyl-sulphonimide. It is made from toluene, which is sulphonated to give *o*-toluene sulphonic acid. This is converted to the amide and oxidised to produce *o*-benzoyl sulphonamide, which yields saccharin :—

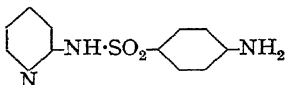


It is about five hundred times sweeter than sugar, but, unlike sugar, possesses no nutritive value, and is useful as a sugar-substitute for diabetics.

In the treatment of pneumonia, blood-poisoning, wound infections, many major diseases and streptococcal infections generally, we have recently heard much about what are known as "sulphonamide" drugs.

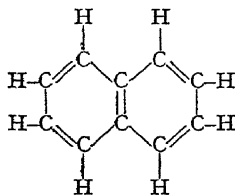
The most publicised of these sulphonamide derivatives was "Prontosil", and it was found that, in the body, the complicated Prontosil molecule broke down into an equally active but simpler substance, *p*-aminobenzene sulphonamide or sulphanilamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{NH}_2$ , which has long been known to chemists. Unfortunately, this simple substance, and also Prontosil, may have certain physiological drawbacks, in that it damages the bone-marrow, so a search was made for compounds of allied structure which incorporate the same beneficial properties, but free from the disadvantages of sulphanilamide.

Two outstandingly successful compounds have been synthesised, which are named sulphapyridine and sulphathiazole; of these the first-named has become justly famous under the title M and B 693; here is its structure:—

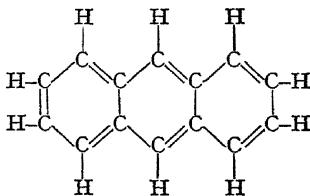


M and B 693.

Two more very important hydrocarbons are obtained in the distillation of coal-tar; they are naphthalene and anthracene. Naphthalene is  $\text{C}_{10}\text{H}_8$  and anthracene is  $\text{C}_{14}\text{H}_{10}$ , and they have the following structure:—



Naphthalene

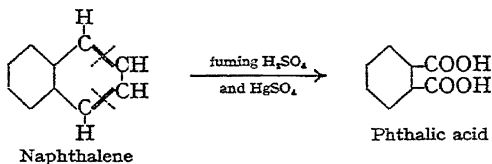


Anthracene

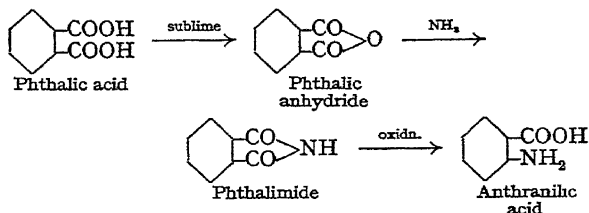
Both these substances behave very similarly to benzene; they may be sulphonated, nitrated and substituted

generally in the same way. Many important dyestuffs have, as their parent substance, naphthalene or anthracene derivatives. Two such dyes, characteristic of naphthalene and anthracene respectively, are indigo and alizarin. Both are of great interest, because they are typical examples of dyes formerly derived exclusively from natural sources, but which have been entirely supplanted by the synthetic, man-made product without any loss in quality, but with great improvement in cheapness, consistency of composition and much greater certainty of control over the operation of dyeing.

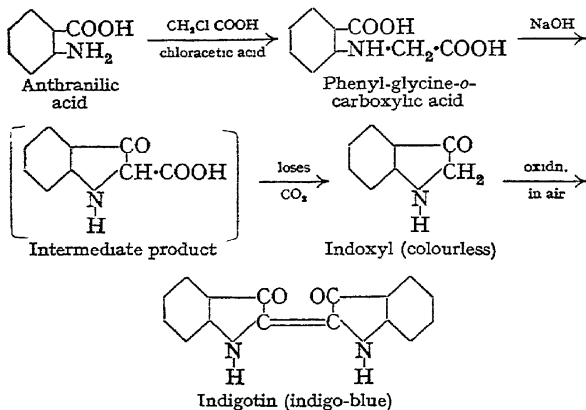
Let us first consider indigo, which is the familiar blue dye used for many types of woollen cloth. The chief constituent of the natural indigo dye is called indigotin, and its main source used to be the indigo plant. Using naphthalene as a starting material, this is oxidised to phthalic acid by means of fuming sulphuric acid, in the presence of mercuric sulphate as a catalyst :—



The phthalic acid is sublimed to give phthalic anhydride, which is then heated in a current of ammonia which converts it to phthalimide :—



By treatment with a hypochlorite such as bleaching powder, the phthalimide is oxidised to anthranilic acid, which is the real starting-point. Anthranilic acid and chloracetic acid are then condensed together, and the product, phenyl-glycine-*o*-carboxylic acid, fused with alkali to give indoxyl. Finally, when exposed to air, and thus oxidised, the colourless substance indoxyl passes into indigotin, the intense indigo-blue dye.



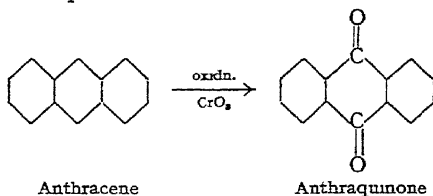
Indigotin is insoluble, but it may be bleached into a soluble form by reducing it with calcium hyposulphite; this soluble colourless substance is called indigo-white. The fabric is steeped in a solution of indigo-white and then exposed to the air; gradual oxidation converts the colourless form of the dye back into the intensely blue indigotin, which is firmly incorporated in the fibres of the material. This process, which is used when dyeing with many dyestuffs, is known as vat-dyeing.

Tyrian purple, a dye highly esteemed by the ancients, was made on the Mediterranean coast near the city of

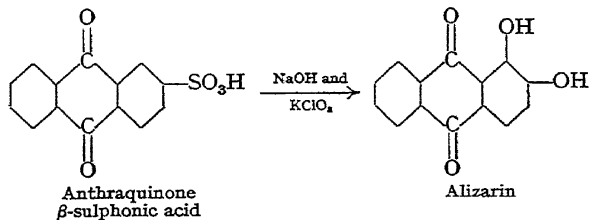
Tyre. It was extracted in minute quantities from large quantities of a certain kind of shell-fish; the reputed cost of production in Roman times was about £60 per ounce. Small wonder wearers of this colour belonged to the restricted circle of royalty. On investigation, tyrian purple proved to have the constitution of dibrom-indigotin, and can readily be produced synthetically.

Alizarin is another dyestuff formerly derived solely from natural madder-root, and known by the name of "Turkey-red".

Anthracene is the starting point in its manufacture; this is oxidised with chromic acid, or electrolytically, to give anthraquinone :—



Anthraquinone, when treated with fuming sulphuric acid, is converted into anthraquinone- $\beta$ -sulphonic acid, which when fused with a mixture of caustic soda and potassium chlorate is converted into alizarin, or 1:2-dihydroxy anthraquinone.





This substance, alizarin, is insoluble in water, and has no affinity for cotton fabrics. The dye must, therefore, be attached to the fibres by means of some intermediate substance, called a mordant (see p. 118), which is deposited in and around the hollow fibres of the cloth. Mordants are usually metallic oxides or hydroxides, such as aluminium hydroxide or ferric oxide, and are feebly basic. The fabric is dyed, after first being mordanted, by being soaked in a warm suspension of alizarin in water. Chemical combination takes place between the slightly acid dye and the feebly basic mordant to give an insoluble coloured compound, called a lake. Using a ferric oxide mordant, alizarin forms a violet lake; a bright red lake, Turkey red, is produced by the use of an aluminium hydroxide mordant.

## CHAPTER XIV

### SYNTHETIC PRODUCTS

IN this chapter, we propose to give some account of those materials, familiar everywhere in our daily lives, which have been deliberately invented by chemists to fulfil some specific purpose.

Many of these substances are being used in place of certain naturally occurring materials because either the natural product is unobtainable in sufficient quantity or, more usually, because the physical properties of the synthetic substance, as it is called, have been deliberately chosen, and even emphasised, in order to provide the maximum degree of usefulness in the field chosen for their application. In many cases, the synthetic product is the result of a deliberate attempt to imitate some rare natural material. Thus, celluloid resulted from efforts to produce a synthetic horn; cellulose acetate, such as safety film and "Cellophane", was the outcome of trying to reduce the inflammability of celluloid. Moreover, it is intended to show that these synthetic products have been "made to measure" in such a way that their internal molecular structure endows them with the very properties which are their characteristic attributes. In this way, these substances have been built up so as to possess all the advantageous properties of the naturally occurring material without those disadvantages so generally characteristic of natural raw materials.

Typical synthetic products, the invention of the chemist, which are foremost in the minds of most people nowadays, are plastics and artificial silk. Both these are substances put to a wide variety of uses, and they will now be considered in turn.

Articles in daily use which are made of "plastics" are

familiar to all; for example, combs, toothbrushes, beer-bottle stoppers, picnic cups and saucers, the telephone, films, ashtrays and toys. In addition, the industrial uses of these materials is widespread, since they take their place in the manufacture of electrical instruments and accessories, radio sets, gears, bearings, lacquers and varnishes. The name "plastics" is, at first sight, something of a paradox, since the characteristic property of the articles made from these materials is that they retain their shape and are by no means plastic, as we know and handle them. However, in the course of manufacturing the article, the material from which it is made is capable of being made to flow, under the influence of heat and pressure, hence under suitable conditions it was once plastic, but retains its shape permanently when restored to natural conditions.

As may be gathered from this, the bulk of plastic articles are made by the process known as moulding. This operation is carried out in special presses, such that the moulds can be heated as the pressure is applied, followed by cooling after moulding is completed.

The wide range of industrial plastics can be broadly divided into two categories, the thermo-plastic and the thermo-setting products. Thermo-plastic materials can be softened and re-softened repeatedly by the application of heat and pressure, provided they are not heated to such an extent that chemical decomposition takes place.

Thermo-setting plastics undergo chemical change when subjected to heat and pressure. This converts them into an infusible and insoluble condition, so that they cannot be further re-formed by the application of more heat or pressure.

These two main classes can be conveniently subdivided into certain chemical families of plastic, depending on their chemical composition or mode of preparation.

Thermo-plastics include the cellulosic plastics such as celluloid, cellulose acetate and the cellulose ethers, also those truly synthetic materials, the vinyl, styrol and

acrylic acid derivatives. Bituminous and wax compositions, as well as natural resins like shellac, may also be included.

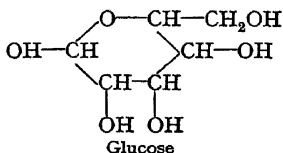
Thermo-setting plastics include the "phenolics" which are obtained by condensing a phenol with an aldehyde, the amino-plastics resulting from the condensation of urea (or one of its derivatives) with an aldehyde, and the glyptals produced by the interaction of glycerin and phthalic anhydride. Although not strictly thermo-setting plastics, the casein plastics, which are obtained from milk, can be included under this heading. These materials can be formed into sheets, rods and tubes by the application of heat and pressure; they can also be moulded very readily.

We are now in a better position to outline the underlying chemistry of the constituent materials and the preparation of the raw plastic product.

Apart from such naturally occurring thermo-plastics as bitumen (used for beer-bottle stoppers) and shellac (for gramophone records), the pioneer material of this class is celluloid. This is made by mixing nitrocellulose with camphor and alcohol.

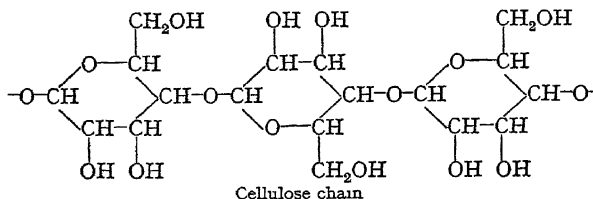
The essential raw material is cellulose, a product of nature, and is the main constituent of cotton, wood, flax, hemp and straw. The cellulose molecule is in the form of a long and complex chain; it is closely related to the sugar glucose.

Glucose has this formula :



and a part of the cellulose molecule is built up in this form :

**F** (Chemistry)



but its total length is such that it includes about 120 glucose units. It can readily be understood why a long molecule such as this forms threads and fibres characteristic of cellulose.

On being treated with a mixture of concentrated nitric and sulphuric acids, certain of the hydroxyl (OH) groups are replaced by  $\text{-NO}_3$  from the nitric acid; this process is called nitration. Hydrogen from the nitric acid unites with the  $\text{-OH}$  group to form water, which is taken up by the sulphuric acid. The degree of nitration (*i.e.* proportion of OH groups converted to  $\text{-NO}_3$ ) depends on the concentration of the sulphuric acid. The number of nitro-groups introduced into the molecule influences progressively the properties of the product, although nitro-cotton, as it is also called, looks no different from the raw cotton. After nitration, the nitro-cotton is washed to remove acid, and finally dried by means of alcohol.

From the nitrocellulose produced in this way celluloid is obtained by mixing it, or, more correctly, dissolving it in a mixture of camphor and alcohol, the proportions of which are carefully regulated.

Camphor forms a "solid solution" with nitrocellulose, and acts as a "plasticiser". Its purpose is to act as an internal lubricant to the molecules, so as to render the plastic capable of being moulded and worked. It has the effect of modifying such physical properties as flexibility, hardness, water and weather resistance, inflammability and electrical properties.

Another cellulose plastic of greatly increased im-

portance is one which does not possess the disadvantage so characteristic of celluloid—namely high inflammability. This product is cellulose acetate, and its molecular structure is such that the acetyl group,  $\text{CH}_3\text{CO}\cdot\text{O}-$ , is substituted in place of certain of the hydroxyl groups in the raw cellulose, and which in nitrocellulose are nitrated.

Purified cellulose, in the form of cotton linters, is treated at about ice temperature with a mixture of glacial acetic acid and concentrated sulphuric acid. As the reaction gives out heat, the mixture is cooled by means of refrigerating plant, otherwise decomposition would take place. The cotton fibres disappear, and the end product is a syrupy liquid. To this, excess of water and alkali are added to neutralise the acid present, and the whole mixture allowed to stand or ripen for three days. In the interval, the acetyl cellulose hydrolyses or saponifies to some extent, losing some of its acetic acid and, on adding more water to the mixture, the cellulose acetate is precipitated from solution as a white matted powder. After thorough washing it is dried. The cellulose acetate produced in this manner is soluble in acetone. The main purposes for which it is used are plastics, films, lacquers and, by no means least, in the manufacture of artificial silk or Rayon.

The provision of suitable plasticisers for cellulose acetate has proved a good deal more troublesome than for the nitrate. Most generally used are compounds containing the phosphate radicle, such as triphenyl or tricresyl or tributyl phosphate.

Another class of thermo-plastics of more recent introduction is the vinyl and styrol products, also the acrylic ester plastics. These materials are all characterised by their glass-like transparency, and are therefore sometimes known as "organic glasses". The vinyl and styrol resins are produced by a process known as "polymerisation", which is dependent on the power of the carbon atom to combine with itself. The simple

hydrocarbon ethylene,  $\text{CH}_2\text{:CH}_2$ , can, under suitable conditions (*e.g.*, action of ultra-violet light or catalysts), be induced to combine with itself or "polymerise" into a complex solid which has the empirical formula  $(\text{C}_2\text{H}_4)_n$ .

Styrene is a liquid having a formula  $\text{C}_6\text{H}_5\cdot\text{CH}=\text{CH}_2$ , and is thus ethylene in which one hydrogen atom has been replaced by the phenyl radicle  $\text{C}_6\text{H}_5\cdot$ . It is obtained commercially as a by-product from the oil industry. By the use of catalysts or "accelerators", this liquid can be polymerised on heating into a glass-like resin which is remarkably clear and light. It finds extensive use in the radio and electrical industries.

Vinyl resins have similar physical properties and may be considered chemically as polymerised derivatives of vinyl alcohol,  $\text{CH}_2\text{:CH}\cdot\text{OH}$ .

By starting with acetylene, derived from calcium carbide and water, and acetic acid, we can obtain vinyl acetate,  $\text{CH}_2\text{:CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ . By polymerisation this yields a clear resin.

Similarly, vinyl chloride,  $\text{CH}_2\text{:CHCl}$ , can be polymerised with itself or with vinyl acetate into a resin having remarkable water-resisting properties, and consequently very useful as an insulator in electrical work.

The methacrylic ester resins are produced in similar fashion. Acrylic acid has the formula  $\text{CH}_2\text{:CH}\cdot\text{COOH}$ , and the derivative most frequently used is the methyl ester of methacrylic acid,  $\text{CH}_2\text{:C}(\text{CH}_3)\text{CO}\cdot\text{O}\cdot\text{CH}_3$ .

On being polymerised, the glass-clear resin which results is known as Perspex or Diakon, according to the form in which it is sold. The remarkable optical properties of Perspex have led to its use in the mass production of cheap lenses and prisms by moulding.

Amongst its advantages over glass are cheapness, lightness and reduced danger of breakage.

A widely used and old-established plastic which falls between the two main classes of thermo-plastic and thermo-setting products is casein plastic.

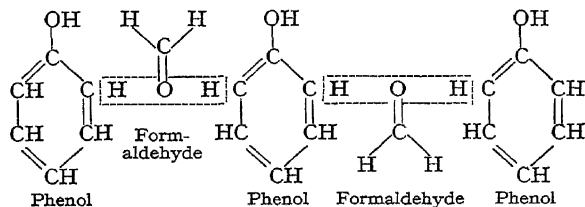
The raw material is a product of nature, namely milk.

Casein exists in milk, combined with calcium, in the form of a suspension. This calcium caseinogenate is a complex protein, and is separated from the milk by means of a coagulant, usually rennet, as in cheese-making. Whey, the clear liquid remaining after the curds or casein have been allowed to settle, provides a source of lactose, or milk-sugar, used in manufacturing baby-foods.

Articles made from casein plastics are produced in two stages. First, the casein is dried, finely ground, sieved and mixed with dyes and fillers to increase its bulk. It is then moulded by means of heat and pressure. Up to this stage the casein is thermo-plastic, but it is finally hardened and rendered infusible by means of a bath of formalin. This is a 40 per cent. solution of the gas formaldehyde ( $\text{H}\cdot\text{CHO}$ ) in a mixture of water and methyl alcohol. The action is very complex, and takes some time, but it is closely akin to the process known as "condensation", which is more fully described in the next section.

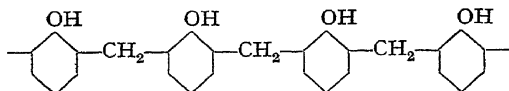
The remaining class of plastics is the thermo-setting products which comprise the phenol-formaldehyde resins, amino-plastics and the glyptals.

The phenol-formaldehyde resins are characterised by Bakelite, a household name. In their simplest form they are made by the interaction of carbolic acid (phenol) and formalin. The reaction is of some chemical interest, as it is typical of a phenomenon known as "condensation", previously referred to. In its simplest form it may be represented as follows :—

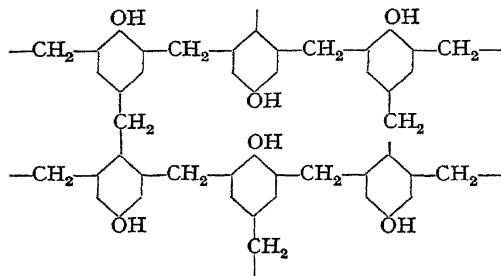




It will be seen that water is eliminated and the condensation product is in the form of a long chain, thus :—



The reaction is carried out in the presence of a catalyst, such as ammonia or sulphuric acid, and at first yields a liquid resin. On standing, a further change takes place, known as curing, in which the resin becomes solid and its molecular structure correspondingly more complex, something as follows :—



in which the long chains are linked in a sideways direction as well, to give added stability.

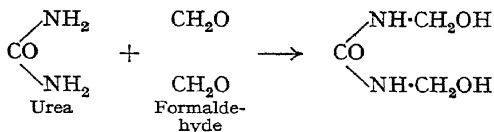
These phenol-formaldehyde plastics are used for a very wide range of products, which include lacquers and varnish, as well as mouldings.

The amino-plastics are condensation products of urea, or one of its derivatives, and an aldehyde, such as formaldehyde. Moulded products typical of this class of plastics are the brightly coloured picnic sets and other household accessories now so common.

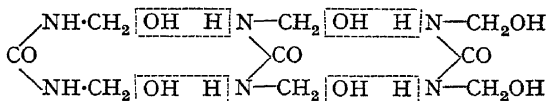
The reaction is somewhat complicated and also takes

place in two main stages. Urea is dissolved in formalin, and the solution heated and the water distilled off.

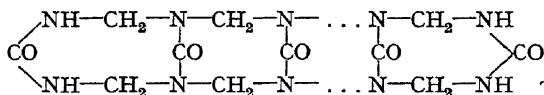
In the first stage of the reaction, the urea and formaldehyde unite and some molecular rearrangement takes place to form an intermediate product, possibly thus :—



This intermediate product then condenses with the elimination of water to form a complex network built up on the following plan :—

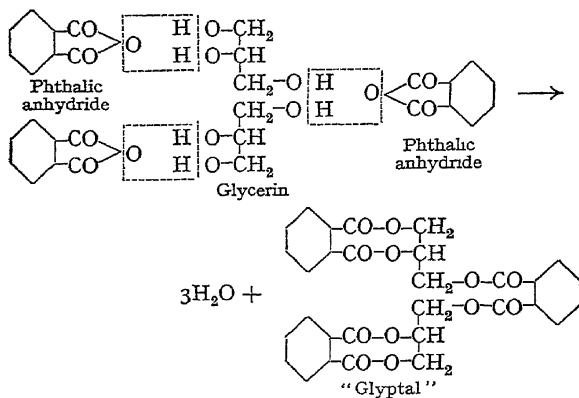


which ultimately would give :—



The last of the synthetic resins to be considered are the glyptal or glyceride resins. They are formed by the reaction of a polyhydric alcohol, such as glycerin, with a polybasic acid or its anhydride, such as phthalic acid. The resulting resins are of great industrial importance in the production of varnishes and lacquers rather than for moulding purposes. An example of the simplest form of this reaction is in the production of glycerin phthalate, which is the resin which results from the

interaction of two molecules of glycerin with three of phthalic anhydride.



It seems probable that further polymerisation takes place to produce a considerably more complex molecular structure.

As a result of systematic examination, it has been found that certain chemical features of the structure of the molecules are responsible for definite physical properties in the material. This is equally true for naturally occurring substances as well as synthetic products. It has therefore been possible for chemists to build up molecules of plastics in such a way as to give added emphasis to those properties in which they are interested and even to suppress those which are detrimental. In this way, they can synthesise materials, which, for the purpose in view, are really "made to measure".

We have seen how artificial resins of the phenol-formaldehyde type (Bakelite) ultimately acquire a net-like structure, at the same time becoming infusible and

insoluble. Something similar can be done to the vinyl and styrol resins by introducing a small quantity of a "copolymer", divinyl benzene ( $\text{CH}_2\text{:CH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\text{:CH}_2$ ), which, as may be seen, possesses two double bonds, and so can link up in two directions.

Another attempt to improve upon nature is to be seen in the "artificial silk" now so much a part of the clothing of our every-day lives. There are four kinds of artificial silk and they all are based on the method of converting raw cellulose, which may be in the form of wood-pulp or cotton linters, into solution, and then regenerating it in the form of a fine thread. They are known as the chardonnet (cellulose nitrate), cuprammonium, viscose and cellulose acetate processes. A very brief outline of the chemistry of these processes is of some interest. The product of the first three of these processes is cellulose in the form of a thread; the last, characterised by its fineness of thread, consists of cellulose acetate.

All these varieties of artificial silk differ considerably from real silk, which is a protein, in that they contain no nitrogen. Real silk contains about 17 per cent. of nitrogen.

Chardonnet silk, named after its inventor, was at first a commercial failure. The cellulose is nitrated as described on p. 162 and the nitro-cotton or collodion dissolved in ether-alcohol. The solution is then forced through fine jets into a warm chamber. The threads harden and they are then "de-nitrated" by reduction with calcium hydrosulphide.

Cuprammonium silk is produced by dissolving cotton linters in cuprammonium hydroxide and squirting the solution into a bath of dilute acid or alkali. The process is illustrated by the following experiment. To a solution of copper sulphate add caustic soda until precipitation is complete and the solution is alkaline. The precipitate consists of copper hydroxide; wash it thoroughly. Add this precipitate to concentrated ammonia solution in which it will dissolve forming a deep blue solution. Into

this solution place a piece of cotton-wool and watch it first gelatinise and then dissolve. Pour this solution into an excess of dilute hydrochloric acid. The precipitate produced is amorphous and consists of cellulose without the fibrous structure characteristic of cotton-wool.

Viscose silk is made from either cotton linters or wood pulp which is first treated with caustic soda and then with carbon disulphide. The result is a thick yellow syrupy liquid consisting of cellulose sodium xanthate, with a formula  $(\text{NaS}-\text{SC}-\text{O}-\text{C}_6\text{H}_5\text{O}_4)_n$ . This compound may be regarded as an example of a cellulose ester. On being treated with special reagents, for example ammonium chloride solution or dilute sulphuric acid containing a little sodium sulphate and glucose, it is re-converted into cellulose. Acetate silk, which includes Rayon and Celenese, is made from an acetone solution of cellulose acetate. We have already described the preparation of cellulose acetate on p. 163 above.

In discussing plastics, we have indicated how, in many instances, they have been built up chemically so as to have physical properties suitable for the purpose for which they are destined.

Silk is a protein, and consists of long, chain-like molecules, of which the oft-repeated links may be represented

by  $\diagup\text{CH}-\text{CO}-\text{NH}\diagdown$ . This is called the "polypeptide linkage"; it is characteristic of the general class of bodies called proteins. Suffice it to say that protein-like substances have been synthesised using this basic plan.

In an effort to improve upon natural silk, which consists of the  $-\text{CO}-\text{NH}-$  grouping alternating with a single  $-\text{CH}-$  group, chemists have evolved substances called "super polyamides". These are built up by combining long-chain molecules, having the characteristic  $-\text{COOH}$  group of an acid, with other big molecules terminating at each end with the amino-group  $-\text{NH}_2$ . The acid molecules "condense" with the more alkaline amines,

eliminating water, and produce a polypeptide link between the two long chains.

All sorts of arrangements are possible by varying the lengths of chain in the acid and amine molecules before condensation. Further, by investigating the relationship between physical properties, such as tensile strength and spinning quality, with the length of the constituent molecular chains, it was found possible to build up a substance having properties vastly superior to real silk both in strength, elasticity and resistance to water.

One of these substances described above is known commercially as "Nylon", and represents a great triumph of deliberate molecule-building by the chemist, so as to yield a product having just the properties desired.

It is prepared by condensing together hexamethylene diamine and adipic acid by heating them together, under pressure. Both these starting materials are derived from phenol,  $C_6H_5OH$ , by catalytic reduction and after-treatment.

Adipic acid has the structure  $COOH \cdot (CH_2)_4 \cdot COOH$ , and hexamethylene diamine is  $NH_2 \cdot (CH_2)_6 \cdot NH_2$ ; the condensation product is built up of recurring units having a structure:—



Nylon is spun by drawing threads from the molten mass, in an atmosphere of nitrogen; the resulting threads are then cold-drawn, which increases their tensile strength, until they have increased in length four-fold. They can be made finer, stronger and more resistant to chemical action than natural silk.

object of the process called dehydration, now so much heard about, and truly wonderful feats of bulk reduction have been achieved, particularly when operating on potatoes and other vegetables rich in water. The process is not the same as simple drying, which takes place in such a manner that the food being dried suffers some change not to our advantage, but water is removed so quickly that no deterioration takes place. Consequently, by adding water when needed, the original foodstuff can be reconstituted, and so restored to its original form.

All chemical processes on which life depends make use of water; the removal of water from living matter is the surest means of stopping the continuation of life. Thus, dehydration helps in the preservation of foodstuffs, as well as rendering them easier to store, since it takes away water necessary to the continuation of the life of the moulds and bacteria responsible for the decay of foods.

The fact that water is the nearest approach to a universal solvent enables it to participate in an astonishing variety of chemical reactions. The body-fluids, particularly blood, consist very largely of water; they carry the food supplies and salts to every part of the organism, and take away the waste products.

By adding water or taking it away from chemical compounds of a complex nature (either in the form of water, as such, or as its constituent elements, oxygen and hydrogen), such as those on which life depends, it plays a vital part in splitting complex bodies into simpler ones or, alternatively, building up complex bodies from more simple components. This controlled breaking down and building up which goes on inside living matter are vital links in the chain connecting higher and lower forms of life. Higher forms of life, particularly the human race, are continuously dependent on more lowly forms of living matter for the continuance of their existence.

Returning to the chemical classification of foodstuffs into carbohydrates, fats and proteins, it is instructive to see what is the composition of some of the common foods we eat and the relative proportions of each constituent. At the same time, it is instructive to see how much water we eat with our food, in addition to that which we drink.

The following table shows quite clearly those food-stuffs which are the main source of any particular chemical class

Foodstuff.	% Water.	% Carbo- hydrate.	% Fat.	% Protein.
Beef . . .	46	—	24	26
Chicken . . .	67	—	7	24
Herring . . .	60	—	10	26
Milk . . .	87	4.5	4	3
Butter . . .	13.5	0.5	83	0.75
Margarine . . .	9	—	83	1.3
Cheese . . .	32	—	27	33
Flour . . .	13	75	0.75	9.5
Peas (dried) . . .	13	55	2	21
Potatoes (raw) . . .	77	20	0.1	2
Nuts . . .	5	10	55	18
Apples . . .	82	12.5	0.5	0.4
Egg-white . . .	86	—	0.25	12.5
Egg-yolk . . .	51	—	32	16
Bread (white). . .	40	51	1	6.5
Oatmeal . . .	5	65	10	14.5

of food. Thus, carbohydrates are of exclusively vegetable origin, fats are either vegetable or animal (and this includes fishes as animals), whilst proteins come mainly from animal sources, although vegetable foods yield them in smaller quantities.

Before proceeding to the details of the main food groups, we must first indicate what, in chemical terms, is meant by the names given to those groups.

Carbohydrates consist of carbon, hydrogen and oxygen—hence their name—and include such substances as sugars, starch and cellulose, all typical of plant life.

Fats also consist of carbon, hydrogen and oxygen, but chemically their make-up is different from carbohydrates



in that they are produced by the union of glycerin and fatty acids. Such compounds are called esters or glycerides. Fats, either liquid oils or solid, may be either of animal or vegetable origin. When obtained from vegetable sources they are extracted from the seed or fruit, in which they act as a store of food on which the young plant can live until it becomes self-supporting. Animals, too, store fats until they are needed; this aspect will be discussed later.

Proteins are also, in the main, of animal origin, but, fundamentally the vegetable proteins are of paramount importance, since it is from them that animals derive their supplies. Animals are unable to build their own proteins from their constituent elements. Instead, they are synthesised by plant life, which is consumed by animals as food, and thus used by animals for their own purposes, being first broken down into simpler substances and then reconstituted into complex animal proteins.

Chemically, the proteins contain carbon, hydrogen, oxygen, nitrogen and, sometimes, sulphur and phosphorus. They are built up from complex amino-acids and polypeptides.

The main sources of protein, in normal human diet, are the flesh of animals and fish, also milk, cheese, and eggs. Certain vegetable foods, notably peas and beans, contain a fair proportion of proteins, but these sources are by no means as rich as foods of animal origin.

When eaten and digested, these three food groups perform differing functions. The carbohydrates and fats are mainly used as fuels in order to keep the body warm and supply it with energy for performing all kinds of muscular work.

Proteins furnish the raw material which, in growing children, is used in body-building and for keeping the adult body in a good state of repair. When necessary, proteins may be used as fuel, but, as they are more valuable than carbohydrates and fats, the body makes every effort to avoid this. Some waste is bound to take place in the breakdown of the proteins, and this releases

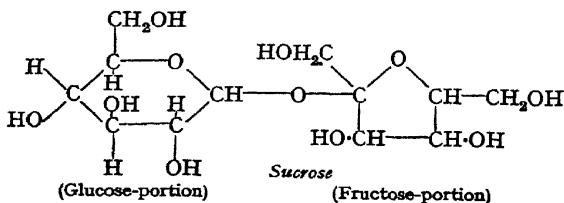
energy to supplement that normally derived from carbohydrates and fats.

Let us now look, in some greater detail, at the chemical composition of a few typical foodstuffs, and also at the structure of their constituent chemical compounds.

Sugar and starch are typical carbohydrates. Starch is an exceedingly complex substance, the formula for which cannot be given, but it is known that it is related to one of the sugars called glucose. This may be shown by adding a little acidulated water to some starch, which is then gradually transformed into glucose, recognisable by its sweet taste.

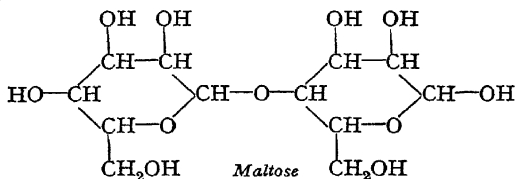
Just as animals put by stores of fat in various parts of their bodies, as a reserve against the time when they are needed, so plants store up the sugars they synthesise. These sugars are converted into a form more suitable for easy storage by being changed into starch. When needed, the plant can easily re-create sugars from the starch reserves. It is for this reason that the reserve stores of foods in roots and seeds, like potatoes, acorns and chestnuts, are in the form of starch.

There are very many sugars known, but commonest, from the point of everyday life, though not the simplest, is cane sugar or sucrose. This sugar is obtained either from sugar-cane, grown in tropical regions, or sugar-beet in more temperate climates. Whatever the source, the substance is the same, having the same chemical composition, taste and mode of crystallisation. Sucrose is itself complex, being built up from one molecule each of glucose and fructose, thus :—

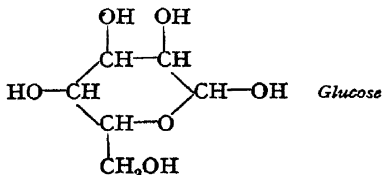


Of the two constituent parts of sucrose, glucose is the better known. It is available commercially and is frequently used as an emergency food, because it is so easily assimilated by the digestive system and its energy is immediately available. As it is readily fermented, to form alcohol, it is used extensively in brewing.

Another sugar, lactose, is found in milk; it is not so sweet as cane-sugar, but is thought to be more suited to infants' digestive systems and, for this reason, is a common constituent of baby-foods. Fructose is contained in many fruit juices, particularly grape-juice, and honey; honey is a mixture of several sugars. Maltose is a sugar present in germinating barley and one of the main constituents of malt. It is more complex than glucose, into which it can be broken down by means of dilute acids. It is from malt that the glucose, used in brewing beer, used to be obtained. Yeast contains a substance, maltase, which rapidly breaks down the maltose into glucose, and another substance, zymase, which ferments the glucose, thus produced, into alcohol. The two glucose molecules of which maltose is made up are linked together thus :—



Glucose itself looks like this :—



Any of the more complex sugars can be broken down into their simpler constituents by warming with dilute acid, such as sulphuric. In nature, the same process is carried out by means of ferments, called enzymes, which have selective action and to which further reference will be made when considering the working of digestion.

Intermediate between starch and sugar is another substance called glycogen; this is a kind of animal starch. Just as plants store away their sugar reserves in the form of starch, having to convert it back into something simpler, like glucose, before being able to use it, so animals store up glycogen in the liver. When needed, it is released and converted into heat and energy, via glucose. Beef and human flesh and muscles contain a small amount of glycogen, but horse-flesh is rich in glycogen. Glycogen is an aggregate of glucose rings; about a dozen are linked together in such a way that they can be fairly readily broken down to make available their energy, when and where needed. Glycogen contains, in addition, phosphorus in some organic combination.

Just as maltose is a combination of two glucose molecules, so starch is an aggregation of many (12 to 15) maltose units. There are even several varieties of starch, all having slightly differing properties. Such variations are probably due to differences in the size of the molecules, that is, in the number of maltose units it contains.

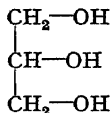
A substance closely resembling starch, but contained in chicory roots and the tubers of Jerusalem artichokes, is called inulin. This is not to be confused with insulin, a substance secreted by the pancreas, which regulates the sugar content of the blood. Inulin is built up from about 30 fructose rings, in contrast to the glucose rings of which starch is formed.

Another important carbohydrate substance which we take in as part of our food, but which has no food value, is cellulose. This is one of the main substances from

which the skeletons of plants are constructed. The cellulose molecule is exceedingly large and complex. Fundamentally, however, it consists of long chains of glucose units (see p. 162); it is particularly resistant to chemical change. Herbivorous animals, which eat much cellulose, are able to break it down to some extent with the friendly co-operation of the bacteria which live in their digestive system. Man, however, has not this facility.

A large proportion of foodstuffs contain fats of some sort. When they are liquid they are called oils, or they may be solid like beef and mutton fat, or half-and-half like butter. All fats and oils, animal or vegetable, have the same general composition; they are compounds of glycerin and fatty acids. Glycerin, or glycerol as it is more correctly called, is a trihydric alcohol (*i.e.*, it has three OH- groups), and its compounds with acids are called esters. Alternatively, the name may be turned the other way and the fats called glycerides, to imply that the fatty acids are combined with glycerin.

The exact nature of the fatty acid in combination with glycerin depends on the kind of fat. The fatty acids consist of long  $\text{-CH}_2\text{-}$  chains terminating in the  $\text{-COOH}$  group characteristic of an organic acid. Glycerin itself has the structure:—



The simplest fatty acid to be found in fats is butyric acid,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ . This is one of the acids which, in combination with glycerin, forms one of the constituents of butter. It is the main cause of the unpleasant smell of rancid butter; it is also present in sweat.

Most of the acids in fats have much longer molecular chains than this; the usual acids are palmitic acid, stearic acid and oleic acid. The first two are characteris-



When any of these fats are treated with hot alkali, such as caustic soda or potash, soaps are formed; the process is also often called saponification. The glyceride is split, or hydrolysed; the fatty acid forms a salt with the alkali, and glycerin is liberated. At the end of the reaction the soap is thrown out of solution by being "salted out" by adding excess of common salt. Hard soaps are sodium salts and soft soaps are potash salts, containing glycerin in addition, since they are not salted out. If olive oil is treated with caustic soda, the result is Castile soap or Venetian soap. Marine soap, which can form a lather with salt water, is made with coconut oil. Another kind of soap is used to make the adhesive on "sticking plaster". Linseed oil and lead oxide are boiled together to produce a "lead soap" which is very sticky, but insoluble in water. Plaster which is coated with this adhesive is, for this reason, sometimes called lead plaster. "Aluminium soap" is used in water-proofing.

The cleansing action of soaps is due to the fact that the alkaline (soda or potash) portion is much more powerful than the fatty acid portion; soaps are therefore feebly alkaline. The calcium or magnesium salts of the higher fatty acids are insoluble in water; thus, when "hard" waters are used, these salts are precipitated, and form the insoluble curd characteristic of hard water washing. The lather, formed by soap, in conjunction with "soft" water, is due to the formation of a colloidal solution, through the "association" (or joining together) of a large number of soap molecules. This solution has the property of "wetting", since it penetrates intimately, in a manner impossible with plain water. Such wetting action assists the mechanical dislodgement of dirt particles.

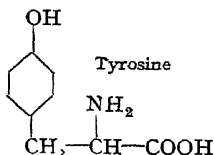
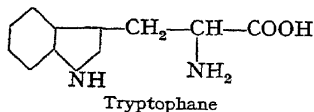
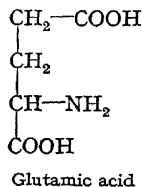
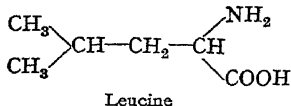
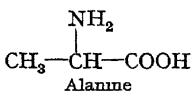
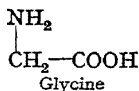
The third group of foods are the proteins, which are either vegetable or animal in origin. The entire animal world is built from proteins; thus, our muscles, flesh, skin, hair and nails are all proteid in composition. The

fundamental unit of living matter is the cell. Inside the cell-walls is contained a watery, gelatinous substance, called protoplasm. This protoplasm, of which all living matter is built, consists essentially of protein, although nobody knows the chemical composition of protoplasm. A little is known, however, about the structure of some of the proteins. Our only way of finding out anything about them is to break them down, under carefully controlled conditions, and examine the breakdown products. Two of the reagents used in this analysis are either dilute sulphuric acid or baryta water,  $\text{Ba}(\text{OH})_2$ ; which reagent is actually used depends on the protein being investigated, and the only guide is experience.

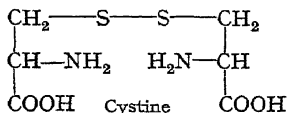
The principal products of protein break-down are amino-acids; these contain the characteristic group

$\text{—CH} \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$ , and thus combine the basic properties of the  $\text{—NH}_2$  (amino) group with the acidic functions of the carboxyl ( $\text{—COOH}$ ) group.

Here are a few of the simpler amino-acids which can be isolated from broken-down proteins:—



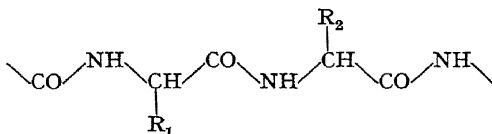




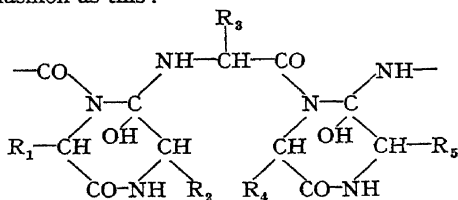
Such compounds as these, possessing dual functions, can combine in a number of ways. They can link up, end to end, to form chains; they can join up sideways and form networks, or they can even unite within themselves, and form "internal salts", by a linkage between basic and acidic groups. In nature, they are found to do all three, thus making protein structure exceedingly complex.

A relatively simple protein, like gelatin, yields at least a dozen different amino-acids; amongst these are: glycine, proline, alanine, arginine, lysine, leucine and several others which have no simple name.

In their simplest form, these amino-acids link together in proteins in such a manner as this :—



$\text{R}_1$  and  $\text{R}_2$  represent the residues of the amino-acids, that part of the molecule attached to the characteristic  $\text{---CH(NH}_2\text{)COOH}$  group. A further variation is introduced when these huge chains link up sideways, in some such fashion as this :—



$R_1, R_2, R_3, R_4$  and  $R_5$  are, as before, residues of amino-acids, which may all be the same or different.

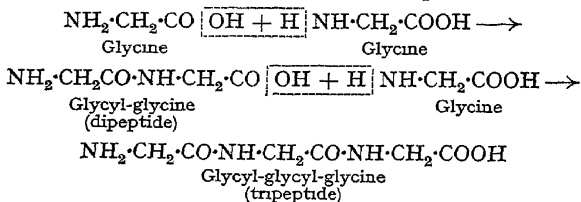
Another kind of cross-linkage is found when the amino-acid cystine enters into the combination. It is characterised by the  $-S-S-$  chain, and is found in natural fibres like hair and wool.

Incidentally, hair, wool, horns, feathers, claws and tortoiseshell are all proteins of a kind called keratin. Not all keratin has the same structure; keratin of mammal origin is different from bird and reptile keratin. This lends additional weight of evidence to the long-known fact that birds and reptiles evolved from a common ancestor, whilst mammals came from different stock.

In view of the vital importance of proteins to our daily life, as well as their interest to chemists, it hardly seems surprising that attempts have been made to build up proteins, synthetically, from their constituent amino-acids. This has proved exceedingly difficult, and only partially successful. The largest molecules which have been assembled are very small when compared with those known to form even the major component parts of natural proteins.

By condensing together amino-acids, so that the acid group of one molecule linked with the basic group of another, the process was repeated as far as it was possible to go. As the molecules became larger they became correspondingly less reactive, and so it was more difficult to make them link up, as desired.

A scheme something like this was adopted:—



Thus, the steps in the series are : dipeptide, tripeptide . . . polypeptide. All contain the characteristic grouping or polypeptide linkage :  $-\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2-$ .

The largest polypeptide so far built up is an octadecapeptide (18-links), consisting of three leucine and fifteen glycine molecules. Its formula is :  $\text{C}_{48}\text{H}_{80}\text{O}_{19}\text{N}_{18}$ , with a molecular weight of 1212.

The average protein molecule is made up of more than a hundred amino-acid molecules and, although we cannot yet reliably determine their molecular weight, the lowest estimate cannot be less than 17,600. There is thus a big gap between the simplest protein molecule and the largest "man-made" polypeptide.

It is interesting to observe that, despite the enormous variety of proteins, the constituent elements are present in remarkably uniform proportions, as shown by the following summary table :—

C.	H.	O.	N.	S.	P.	%.
50.5	6.5	21.5	15.0	0.5	0.42	min.
54.6	7.3	23.5	17.6	2.2	0.85	max.

By way of conclusion, we must consider briefly the inorganic or mineral salts necessary to life and forming part of our food supplies.

Foremost amongst these in importance, undoubtedly, is common salt, sodium chloride. In addition to imparting its characteristic flavour to many foods, it is essential that adequate supplies should be constantly available. Salt is an essential constituent of the blood, and from this source comes the salt found in sweat and tears. These two secretions make a big demand on available salt in the body, and lack of salt may give rise to a kind of cramp in those whose occupation causes profuse sweating. The concentration of salt in the blood is about a third of that in sea-water. The hydrochloric acid forming a part of the gastric juices is derived originally from the salt present in the blood.

The essential nature of salt to animal life is in marked contrast to plant life, to which potash is essential and common salt (sodium compounds) is useless. A trace of some potash salt is necessary for human life, since without it the heart muscle cannot relax and, on the other hand, without a trace of a calcium salt in the blood, the same muscle cannot contract.

Supplies of calcium, but in much larger quantities than the heart muscle needs, are required for bone-building. For the same purpose, also, phosphates are needed. The most valuable natural source of both these substances is milk, hence the wisdom of encouraging growing children to drink plenty. As we shall see, these calcium supplies cannot be properly utilised unless there are adequate amounts of vitamin D available at the same time. Magnesium salts, in the form of phosphate and carbonate, are also used in bone-building.

Iron is another essential inorganic substance which the body must take in. The red oxygen-carrying substance in the blood, called hæmoglobin, contains iron. The body guards its iron supplies most carefully, and wastes none if it can help it. The total amount of iron present in the body, under normal circumstances, is only about  $\frac{1}{10}$  oz. The main source of iron, to replenish losses, such as bleeding, is liver; other foods, such as cocoa, peas, beans and lentils, are also useful. Unfortunately the iron in red meat is mostly in an indigestible form, hence, although the most obvious source, it is not available. Brown bread and eggs also provide iron supplies; milk is poor in iron, and spinach, contrary to popular belief, is poor in iron also. Iron deficiency gives rise to anæmia, the cure for which, in addition to adequate supplies of iron, requires traces of salts of the metals copper, zinc, manganese and cobalt. Copper is essential to the proper utilisation of iron in foods for the formation of hæmoglobin. Zinc appears to be a constituent of insulin, the hormone secreted by the pancreas which controls the amount of sugar present in the blood-stream.

We have already mentioned the all-important sodium chloride; two other members of the halogen family are also required, though not in such large quantities.

Fluorides are to be found, in traces, in the bones and in the structure of the teeth, particularly in the hard enamel outer coating.

Iodine compounds are used to produce the hormone secreted by the thyroid gland, called thyroxin. Deficiency of iodine causes over-development of the thyroid gland, which is situated in the throat, and leads to goitre. As only traces of iodine and fluorine are required for healthy development, adequate supplies usually are available either in drinking water or from fish and vegetables. Both come from the soil which, in its turn, probably obtains its supplies from minute traces of sea-spray which penetrate remarkable distances inland. Only in parts of countries remote from the sea, like Derbyshire in Britain, Switzerland or Central America is there such a shortage of iodine as to cause a universal tendency to goitre. Any iodine deficiency nowadays is usually corrected by the use of iodised table-salt.

## CHAPTER XVI

### DIGESTION AND RESPIRATION

HAVING seen of what chemical substances the foods we eat are composed, we can now try to form an idea of the fate, chemically speaking, which befalls them when they are eaten and digested. Further, we shall see how the body makes use of this raw material to keep itself warm and in good repair and, finally, what chemical changes take place when we breathe, move and do muscular work.

First, let us consider the process of eating and digesting typical members of the three main food groups: carbohydrates, fats and proteins.

We have already made passing reference to the cell as the fundamental unit of living matter. Our bodies are built up entirely of cells, millions upon millions of them; they are not all identical, but are adapted so as to perform numerous special functions. Thus, we have the cells of which skin is made, the red cells in the blood which transport oxygen to all the tissues, the cells of which bone is built, the cells forming our flesh, muscles, blood vessels and intestines. All these cells are separated from one another by a thin dividing wall. This wall is not impervious to all matter, but it is of such a structure that a two-way traffic of supplies is possible; nutrient matter can come in and waste products can get out. Whether or not matter can penetrate the cell walls depends on the size of the molecules of which that matter is composed. Thus, if we take a bag of parchment, to represent the cell-walls, and place in it a mixture of water, salt, starch, alcohol and glue, the whole bag-full can be immersed in some suitable vessel of water. After the lapse of an hour or so, we shall find that there is salt and alcohol present in the water outside the bag, but no sign of the starch or glue. Evidently, the molecules of

salt and alcohol are small enough to get out, through the parchment, but the starch and glue cannot. As we shall soon see, the size of the molecule is of great importance in determining the manner in which the body can absorb the nourishment it needs from the foods provided.

Suppose we consider first the digestion of a starchy food, like bread, porridge or rice-pudding. It is chewed up and, during mastication, much saliva is mixed with it. Saliva contains an enzyme, ptyalin, which acts upon starch so as to break it down into sugars. As we have already seen, starch is built up from large aggregations of glucose units. Not all the starch has time to be converted into sugar before it reaches the stomach, and here, for the time being, no further digestion takes place, because the stomach juices are acid, and the enzyme ptyalin can only work effectively in the presence of an alkali. When it is allowed to pass on into the duodenum, however, it is completely broken down into sugars, such as maltose and glucose, by the pancreatic juice.

The pancreas gland, called the sweet-bread by butchers, secretes a juice which contains enzymes capable of breaking down all three groups of foods, carbohydrates, fats and proteins. In addition, it produces an internal secretion, insulin (which it passes into the blood-stream), which regulates the amount of sugar contained in the blood. The starch-digesting enzyme of the pancreatic juice is called amyllopsin; the other two enzymes, trypsin and steapsin, break down proteins and fats respectively.

As the part-digested starch passes on through the stomach and intestine, the sugar molecules are able to penetrate the walls of the gut and enter the network of tiny blood vessels with which the intestines are richly provided. Thus, the sugars enter the blood-stream and are passed on to the liver, where they are either stored up in the form of glycogen or else used immediately as fuel.

Fats are digested in the intestine by the pancreatic juices and the bile. As we have seen, fats are split up, or saponified, by the soap-boiler into glycerin and the sodium salts of fatty acids. The bile, which contains sodium carbonate and other salts, and also an enzyme called lipase, does something similar. The glycerin and the fatty acids, so produced, each penetrate the intestinal walls in the same way as the sugars. The bile helps this action by forming soluble complex compounds between the bile salts and fatty acids. When in the circulatory system, the glycerin and fatty acids unite together again into fats. It does not necessarily follow that they combine together to form fats of the same chemical composition as before digestion; the new fats formed are characteristic of the human body. It is for this reason that beef fat differs from mutton fat, which again differs from goose fat. The body selects the fatty acids which it requires and combines them with the glycerin, and so produces the fats it needs, and which have the same composition, no matter what were the constituents of the fats in the food. The fats so formed are carried into the lymphatic system, which transports them to those parts of the body where fat is stored until needed, or else they are made available for more immediate consumption.

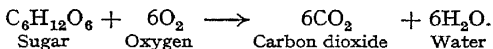
The gastric juices contain hydrochloric acid which has a concentration of up to 0.5%; these check the digestion of carbohydrates and fats, but work on the proteins, which they split into peptides and amino-acids. Pepsin is the chief enzyme which does this work; it requires an acidified medium on which to act, in contrast to ptyalin. On passing on to the small intestine, protein digestion is completed by the action of the enzyme trypsin in the pancreatic juice.

As before, the amino-acids are absorbed by the circulatory system, after passing through the walls of the stomach and intestines; they are carried via the portal vein to the liver, which sorts and redistributes them. Some are used for repairs to muscles, which are always



doing work, and so wearing out. Far more protein is taken in as food than is required for maintenance purposes, so the balance is used as fuel; only 10–15 per cent. of the nitrogen taken in as protein is used for replacements. The ultimate breakdown product of protein is urea,  $\text{CO}(\text{NH}_2)_2$ , whether it is waste from muscular activity or direct consumption as fuel. The urea is carried in the blood stream, and thence, via the kidneys, into the bladder.

The sugars absorbed into the circulatory system are either stored in the liver as the complex compound glycogen, or burned as fuel to keep the body warm. Although there are no visible flames resulting from this burning, the chemical action of oxidation which takes place is the same as ordinary combustion, the difference being one of speed at which the reaction takes place. The sugars are oxidised to carbon dioxide and water, thus :—



The carbon dioxide is carried away to the lungs by the blood, where it is expelled in the breath. The water is separated from the blood by the kidneys, whence it passes into the bladder.

The sugar in the blood, almost the whole of which is glucose, is kept at a very constant level, at about 0.1 per cent., the store of glycogen in liver acting as a reservoir. The internal secretion of the pancreas, called insulin, is responsible for this. When this control breaks down, for any reason, the sugar content of the blood rises, and glucose is found in the urine; if unchecked, the result is likely to be fatal.

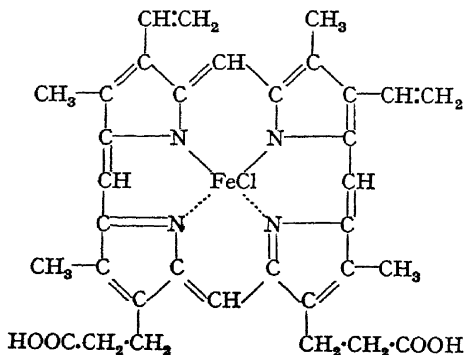
When fats are used as fuel, for which purpose they are the best of any of the foods we consume, a similar oxidising action to that of the sugars takes place.

Something has already been said about the circulation of the blood. We all know what blood looks like, but few realise its great chemical complexity, or the multi-

tudinous tasks which it performs. The average volume of blood present in the body is about a gallon, all told, but this varies with the bulk of the person. Its general function is to transport food materials to the tissues which need them, and remove the waste products to the kidneys, where they are separated and disposed of. More important than either of these functions is the transport of oxygen to the muscles and other working parts of the body, including the brain.

Oxygen is carried by means of a special substance, called hæmoglobin, which combines with oxygen very easily and parts with it just as easily; where the supply of oxygen is plentiful, it takes up oxygen; where the need for oxygen is great (such as where there is an excess of combustible material), it gives up its oxygen. It has been found that one pint of blood can carry as much oxygen as is contained in a pint of air.

The blood colouring matter, hæmoglobin, is made up of two parts, hæm and a basic protein called globin. Hæm we know something about; it bears some resemblance, structurally, to chlorophyll, the green colouring matter in plants. This is supposed to be the formula of its chloride :—



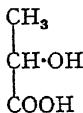
Globin is, at present, of unknown constitution, but it is known that hæmoglobin from different animal sources differs in the globin portion of the molecule.

The red colour of blood is due to oxyhæmoglobin; hæmoglobin itself is purple. The characteristic colour of hæmoglobin may be demonstrated by dropping a little blood into water and adding a small crystal of a reducing agent, such as sodium hydrosulphite. The oxyhæmoglobin in the blood will be reduced, and the colour of the mixture turns purplish. Shake it up with fresh air again for a little while, and it will gradually return to its familiar red colour, due to re-oxidation. The hydrosulphite must be completely oxidised before the effect can be seen.

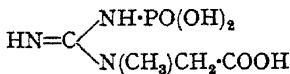
If, instead of shaking up the reduced blood with air in order to reoxygenate it, we bubble coal gas through it, it will also turn red. The red colour is somewhat brighter than that of normal blood, and, this time, we cannot reduce it with hydrosulphite. The reason for this is that the hæmoglobin has combined with carbon monoxide in the coal gas and become carboxyhæmoglobin, which is a much more firmly united compound. It does not decompose easily, like the oxy-compound. Thus the oxygen-carrying capacity of the blood has been lowered, or even totally lost. This is what happens in coal-gas poisoning. The body cannot work properly because the tissues, muscles and other organs have been deprived of their oxygen supply, because the blood is no longer capable of carrying it.

The circulation of the blood allows supplies of all sorts to be carried to every part of the body; it is, in fact, the main line of communications. We have seen that glycogen is stored in the liver, but it is actually utilised by the muscles, being transported by the circulatory system as glucose. The muscles contain a large amount of water, some protein and a small quantity of glycogen, and traces of at least three other substances. These remaining three substances are lactic acid (I), a phosphate

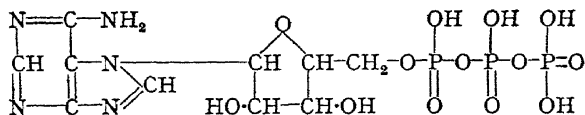
of a sugar (called ribose) combined with adenine (II) and a phosphate of creatine, an amino-acid (III).



I. Lactic acid



III. Creatine phosphate



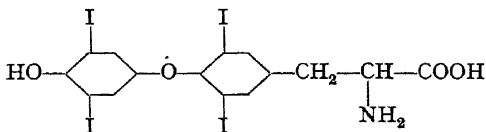
II. Adenyl pyrophosphate

Whether at rest or working, the muscles are taking up oxygen and giving off carbon dioxide, derived from the oxidation of lactic acid and glycogen. When the muscles are made to work, the amount of oxygen needed is much greater, and it is also found that the amount of lactic acid present increases, due to the breakdown of glycogen. On being allowed to rest, part of this lactic acid, about a fifth, is oxidised to carbon dioxide and water, but the remainder is re-formed, by means of enzymes also present, into glycogen. At the same time as this consumption of glycogen is going on, other reactions are taking place, some of them also reversible. The compound of creatine and phosphoric acid (III) breaks down and, during rest, re-forms. In a similar way, the compound of adenine, ribose and phosphoric acid (called adenyl pyrophosphate, II) breaks down and re-forms ready for the next spell of work.

All these breakings-down and re-formations provide energy, and there are inevitable losses; part of the broken-down constituents are oxidised, and the deficiency has to be supplied from the bloodstream, which also removes the products of decomposition—for the most part carbon dioxide and water.

The uniform temperature of the body, between 98 and 99° F., when in a healthy condition, is well known to all. In contrast to the usual heating devices, which give out more heat the more fuel is added, the body regulates its temperature most skilfully and independently of the food available. The controls are numerous and are, in the main, chemical in action. We have already mentioned one, in passing—namely, the control of blood-sugar content by means of insulin from the pancreas.

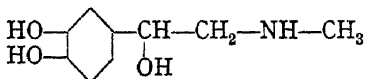
Another most important gland has also been noticed, when speaking of the importance of iodine in the maintenance of good health. This gland is the thyroid, and its characteristic secretion contains thyroxine. It has been investigated chemically, and has proved to be a relatively simple compound, which can now be made synthetically. We are therefore rendered independent of supplies derived from natural sources, such as the thyroid glands of cattle. Here is its formula; it will be seen to be related to the amino-acid tyrosine:—



The thyroid, situated in the neck, introduces minute quantities of a thyroxine-protein complex, called thyroglobulin, into the bloodstream, whence it is transported to the organs, such as the heart, which it influences. This thyroid secretion controls the rate at which the body uses up its food supplies, known as metabolism, and hence the speed at which we live. It is therefore a master control.

Another "chemical messenger" is secreted by the suprarenal glands, lying just above the kidneys. This hormone—which is the name given to the whole class of chemical messengers—is named adrenalin, and influences

the blood pressure. It was one of the first hormones to be discovered and its effects investigated. It has been synthesised, and its constitution is :—



It has been observed that certain psychological conditions, such as rage, anxiety or fear, cause the amount of adrenalin present in the blood to increase. This increase in adrenalin is supposed to be responsible for many of the changes that occur in man under the influence of fear or rage, such as blanching of the skin, dilatation of the pupils and even causing the hair to stand on end !

All these chemical controls of the vital functions are frequently duplicated, so that if one fails, for any reason, there is another which takes charge and prevents disaster. Very many of these controls are known, some are understood fairly well, many more without doubt remain to be explained and others have yet to be discovered.

## CHAPTER XVII

### THE VITAMINS

ALL of us have heard of scurvy and rickets, and some also are familiar with other diseases, like pellagra and beri-beri. Characteristic of these complaints is the common fact that they are neither infectious, nor contagious, but seem, instead, to be associated in some manner with the diet of the victims. This is not to imply that such food poisons the sufferer, or even actively disagrees with him, but it does not seem to supply the body with all that it needs for its physical well-being. In other words, actual physical illness arises from the insufficiency or total absence of some substance from the diet. Moreover, such illness can be cured by supplementing the diet with certain special foods, and again, persons normally including those supplementary foods in their normal range of meals are not known to suffer from these diseases.

In general, it has been found that such foods as butter, milk, eggs, yeast, green vegetables, fresh fruit, and also the livers of certain fish and animals, are capable of restoring health to the sufferers from diseases associated with monotonous and restricted diets. It seems that it is amongst these more concentrated foods that we must look for the real substances responsible for maintaining our physical health. Also, the amount of special food needed is only small. During a research on the feeding of animals on carbohydrates and proteins which had been most carefully purified, it was found that the animals suffered from one or more of these diseases, and that certain accessory foods, like milk, eggs or cod-liver oil, cured them. As the chemical composition and constitution of their basic diet was known and was scientifically calculated, it was concluded that the

accessory food contained a minute quantity of some vital substance, and this was termed a "vit-amine".

More experiment indicated that each deficiency disease was associated with a specific accessory food; hence the conclusion was that there ought to be some definite substance the presence of which prevented or cured a particular disease. These chemical substances which have this specific action we now know as "vitamins". They are not amines, as was at first thought when the name was given, but belong to a variety of chemical families. An outline of the sources and action of the known vitamins is of some real interest to us all. They are known by the letters of the alphabet, for the sake of convenience; several have been made synthetically by chemists, and are of known chemical constitution. Much still remains to be discovered. The following vitamins are at present known:  $A_1$  and  $A_2$ ;  $B_1$ ,  $B_2$ ,  $B_3$ ,  $B_4$ ,  $B_5$ ,  $B_6$ ; C;  $D_2$  and  $D_3$ ; E;  $K_1$  and  $K_2$ ; P; P.P.

The vitamins essential to the human diet are A,  $B_1$ ,  $B_2$ , C and D; the others in the list are not quite so important and have mostly come to light in the efforts made to determine the chemical composition and action of the more important ones. Some of these vitamins dissolve in water, and so are liable to get lost during the cooking of foods, particularly vegetables. Other vitamins are only soluble in fats, hence the body must be supplied with them associated with fatty or oily foods.

Vitamin A is complex and its presence assists the body to resist the attacks of infectious disease and epidemics; it helps us to see better in the dark and its absence gives rise to night-blindness. Normal healthy growth of children is impossible without it. Serious deficiency gives rise also to a scaly condition of the delicate membrane covering the eyes, which is called xerophthalmia. The ordinary skin also becomes hard and horny, producing a condition called "toad-skin" or phrynoderma in extreme cases.

Vitamin B is even more complex and has, so far, been



resolved into nine distinct substances. It is associated with the prevention of the disease beri-beri common in the Far East where rice is eaten. Another disease, pellagra, is common amongst people who live on maize, and one of the B vitamins prevents this. Still another part of the vitamin B group is responsible for the healthy working of the nerves and muscles, also for the proper breaking-down and use of the carbohydrates taken in as food. Vitamin C is known to be responsible for preventing scurvy. This disease is common where people are deprived, in their diet, of fresh fruit and vegetables. The limbs swell, the gums bleed and teeth drop out. The minute blood vessels beneath the skin, called capillaries, become brittle and burst; this gives rise to red and purple spots all over the body.

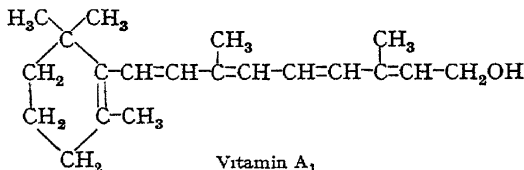
Vitamin D is associated with the prevention of rickets. This disease used to be so common in this country that it was known as the "English disease". Its results are to be seen in people who have bow legs, hunched backs, swollen joints and other deformities. Vitamin D is also responsible for the preservation of the health of our teeth as well as our bones.

Amongst the remaining vitamins which are of subsidiary importance are vitamin E, which prevents sterility in man and many animals. Vitamin K is in some way associated with the formation of the substance which causes blood to clot, and so prevents us bleeding to death from a small cut or scratch. Vitamin P is associated with vitamin C in some way and assists its action in the prevention of scurvy. It appears to influence the permeability of the capillaries, to which we have already made reference.

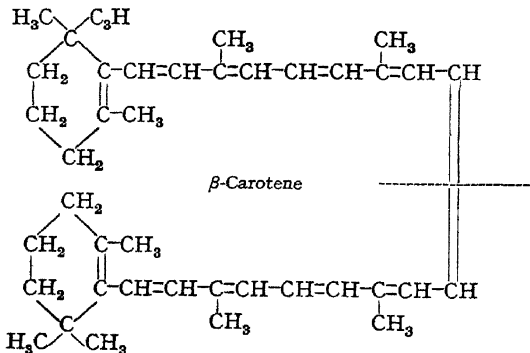
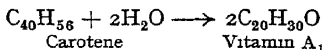
Vitamin A is a complex and consists of at least two substances, known as  $A_1$  and  $A_2$ ; neither is soluble in water, but must be assimilated in oil or fat.

Vitamin  $A_1$  is found in butter, milk, eggs, carrots, spinach and other green vegetables, also in the livers of animals and certain fish. It has been isolated as a pale yellow, viscous oil which has a formula of  $C_{20}H_{30}O$ .

Chemically it is an alcohol; it has been synthesised and has the following constitution :—



The parent substance of vitamin A<sub>1</sub> is the orange-red plant colouring matter  $\beta$ -carotene. This is a hydrocarbon, C<sub>40</sub>H<sub>56</sub>, which is contained in such widely varied forms of life as carrots, green grass, diatoms and marine algæ. The transformation from  $\beta$ -carotene into vitamin-A<sub>1</sub> seems to take place in the livers of animals and fish; it is there that the vitamin is stored. The change is a relatively simple one; the carotene molecule is split, as shown below, and the elements of water added to form the alcohol vitamin A<sub>1</sub> :—



It seems as though once vitamin  $A_1$  or carotene has been formed, perhaps by some small marine animal or plant, it is passed on unchanged. For example, some small fish, which lives on algæ, stores in its liver the vitamin which it derives from the carotene in the food it eats. A larger fish devours the small fish, and with it gets its store of vitamin A. Finally, cod or halibut are caught for human consumption, and their livers provide a source of vitamin-A-rich oil.

Similarly, the carotene and vitamin  $A_1$  in the yolk of egg, which is responsible for the colour, is derived from grass and vegetables eaten by the hen which laid the eggs. Also the cow passes on, in its milk, some of the carotene which it derives from the grass it eats, so giving butter and cream their colour.

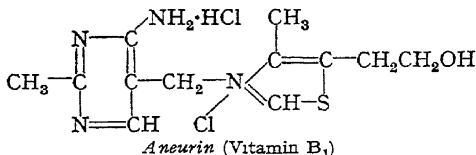
Seasonal variations in vitamin-A content of foods have been observed and traced to a variation in the diet of the hens and cows which produced the foods. The greatest quantities are found in June and July, the lowest amounts in the early part of the year. There can be little doubt that the marked increase in the incidence of ill-health which is associated with the early months of the year is related to these seasonal variations in the vitamin content of foods.

It has been found that the power to see in the dark is due to the formation of a substance called "visual purple" in the retina of the eye. This substance, which is a compound of vitamin A and a protein, is light-sensitive, and is bleached by its action. People short of vitamin A cannot make this compound, and so cannot see properly in the dark.

The livers of certain fresh-water fishes contain a compound closely resembling vitamin  $A_1$  and having properties similar to this substance. It contains two less hydrogen atoms than vitamin  $A_1$  but its constitution is not yet known; it is called vitamin  $A_2$ .

Vitamin B is even more complex, and is known to consist of at least nine components. All are soluble in water.

Vitamin B<sub>1</sub> is associated with the prevention and cure of beri-beri. This disease is common amongst people who live on a diet of rice which has its outer husk polished away from the grain. From the bran from such rice the substance now known as vitamin B<sub>1</sub> was first obtained. It was first isolated as a crystalline hydrochloride of an organic base, and had the formula C<sub>12</sub>H<sub>18</sub>ON<sub>4</sub>Cl<sub>2</sub>S. Its constitution was later proved to be:—

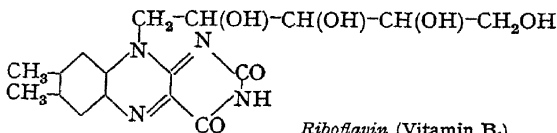


It can be produced synthetically, and is much used in this form because most diets do not contain sufficient of this vitamin. Lack of it may lead to some kinds of neuritis—hence its name.

It has been found that aneurin (B<sub>1</sub>), also known as thiamin, plays an important part in the breaking down of carbohydrates in food, so as to supply the body with heat and energy. In particular, it speeds up the chemical processes in nerves and muscles.

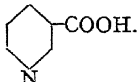
Vitamin B<sub>2</sub> was discovered in tracing the cure for the disease pellagra, in which the skin and intestines become inflamed, and more than one vitamin was found necessary to accomplish this cure; the two principal substances are riboflavin (B<sub>2</sub>) and nicotinic acid (P.P.).

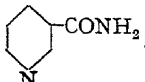
Riboflavin is a yellow pigment found in certain foods, such as milk; its formula is C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>. It has been synthesised, and its structural formula is:—



This substance has been found to be connected with the oxidation of the tissues of the body, and therefore contributes much to the general function of respiration. Its deficiency may lead to one form of cataract.

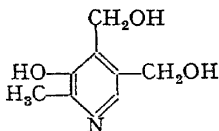
Vitamin P.P. is probably the simplest of the known vitamins. As already mentioned, it is directly concerned with the prevention of pellagra, a disease common amongst people who live on maize. The pellagra preventive (P.P.) was found to be a well-known and simple

substance, nicotinic acid, . It could be

administered in this form or as its amide, ;

it worked just as well. It is unfortunate that our bodies do not possess the power to convert nicotine, derived from tobacco, into nicotinic acid or amide. In the body it is believed to be associated with the breakdown of carbohydrates, in a similar manner to the action of aneurin ( $B_1$ ).

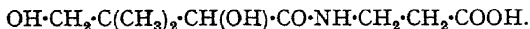
Three further members of the vitamin B complex are now known; they appear to be of minor importance and little is yet understood about human requirements of these three vitamins. The first, vitamin  $B_6$  or pyridoxine, is associated with a deficiency dermatitis resembling pellagra. This vitamin has been isolated and synthesised; its formula is:



*Pyridoxine* (Vitamin  $B_6$ )

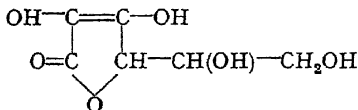
It will be seen to be a derivative of pyridine  $C_5H_5N$ , as is vitamin P.P.

The action of the two other vitamins seems to be concerned with the colour of the hair and in some way assists pigmentation, thus preventing grey hair. It seems too much to hope that grey hair can be averted by attention to diet; rather, it appears, we must expect to go grey in spite of these vitamins. The first of these vitamins is pantothenic acid :



The other is the simpler and long-known compound, *p*-aminobenzoic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ .

Vitamin C, also called ascorbic acid, is another of the more chemically simple vitamins; it was also the first to be synthesised. It was first isolated from fruit juices, and is related to certain of the sugars; this is its formula :—



Ascorbic acid

It dissolves in water, and the solution is feebly acid. The hips of wild roses provide a very rich source of this vitamin.

Associated with vitamin C is another substance, not so well known, which has been called vitamin P, not to be confused with P.P., which is the pellagra preventive nicotinic acid. This additional substance, which was found in lemon juice, seems to be one of the water-soluble yellow plant pigments called hesperidin or citrin. Not much is known about its action or occurrence, but it looks as if it must act in conjunction with ascorbic acid in the cure of scurvy.

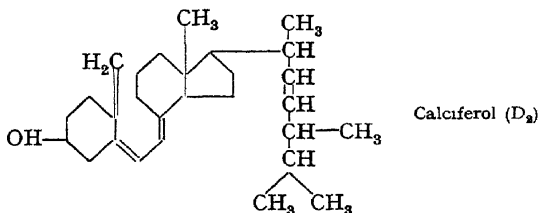
Vitamin D has proved rather a puzzle to isolate, and caused quite a good deal of confusion until recently.

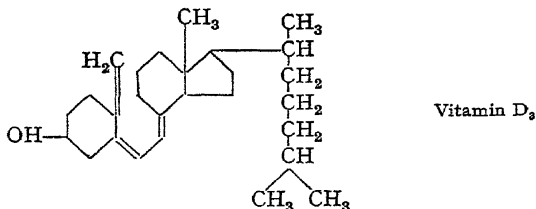
It is known that the bone disease rickets can be cured

in either or both of two ways. Ultra-violet light, also called artificial sunlight, could be used all the year round as a sun-bath, or else the sufferer could be given cod- or halibut-liver oil. A combination of both was better still.

It was found that there was a rickets-curing substance in cod- and halibut-liver oil; this was eventually isolated and its composition determined. Investigation showed that this substance belonged to a class of bodies known as sterols, which are found in the bile, and which are present in minute quantities in the blood and skin. Parallel with these investigations, it was found that if one of these sterols—namely, ergosterol (first found in the drug ergot)—was treated with ultra-violet light, a rickets-preventing substance, named calciferol, was produced. It was concluded from this that the active principle of cod-liver oil and this synthetic product were one and the same thing. Unfortunately, measurements of the activity of the natural and synthetically produced substances showed them to be different, so a different line of approach had to be tried. This led to the discovery that the parent substance of vitamin D (natural) was another sterol called cholesterol.

To avoid confusion it was agreed to call the synthetic vitamin D calciferol or  $D_2$ , and the isolated natural product  $D_3$ . Both are of known structure, but  $D_2$  is the only one which has been synthesised. Here are their structural formulæ for comparison :—

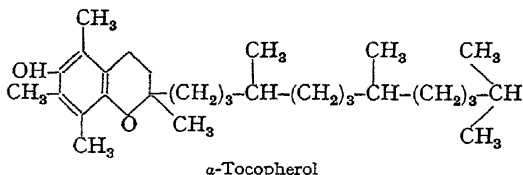




It seems clear that there is more than one natural vitamin D, but little is yet known about the others.

The action of vitamin D in the body seems to be to encourage the absorption into the blood of calcium salts and phosphates. Both these are necessary for building strong bones and healthy teeth. Incidentally, good teeth also need the assistance of vitamin C, as well as D.

A vitamin of fairly recent discovery is responsible for maintaining fertility in man and animals. It is a complex, consisting of at least three substances, which works in conjunction with the pituitary gland. These three substances are known as vitamins E and are  $\alpha$ -,  $\beta$ - and  $\gamma$ -tocopherol. They are alcohols with a formula of  $C_{29}H_{50}O_2$ , all closely related. Only one,  $\alpha$ -tocopherol, has been synthesised and its constitution is :—



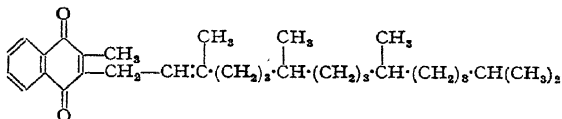
These substances are found in green plant tissues, also in the germ of wheat, which is the best source.

Another vitamin of recent discovery, but of less vital importance, is vitamin K. This substance is associated with the clotting of blood. The ability of blood to clot

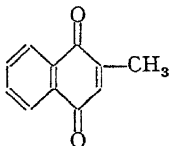


readily is related to the quantity of a substance in it called prothrombin, and it appears that vitamin K is concerned with the process of making prothrombin by the body.

There are at least two substances,  $K_1$  and  $K_2$ , which have been isolated from green plants, and one of them has this structure :—



The other, K<sub>2</sub>, is similar, but possesses a somewhat different side-chain. Both have been synthesised, and have led to an interesting development in which nature has been "improved upon". It was found that the relatively simple compound, 2-methyl-naphthoquinone,



was even more effective than the natural product. It has the added advantage of being cheap and easy to prepare pure. It will be seen that this substance possesses no long side-chains, but contains the same nucleus as the natural compounds. It illustrates one aspect of the vitally important study of the relationship between chemical constitution and physiological properties.

The two tables in the next pages summarise the above information by showing the names of the vitamins, the consequences of their deficiency and the sources from which they may be obtained in nature.

## FAT-SOLUBLE VITAMINS.

Chemical Name.	A <sub>1</sub> and A <sub>2</sub> .	D <sub>2</sub> .	D <sub>3</sub> (Natural.)	E	K <sub>1</sub> and K <sub>2</sub> .
Deficiency causes	— Xerophthalmia. Night-blindness. Toad-skin. Stunted growth	Calciferol. Rickets. Dental decay.	Rickets Dental decay	Toopherol. Sterility.	Phylloquinones. Loss of blood-clotting power
Has been synthesised.	Yes.	Yes.	No.	Yes.	Yes.
Best sources.	Cod- and halibut-liver oils, spinach, eggs, butter, carrots, green vegetables, milk.	Not present in foods.	Eggs, butter, cod- and halibut-liver oils.	Wheat germ, lettuce, green plant tissues.	Spinach, cabbage, alfalfa.

# THE VITAMINS

## WATER-SOLUBLE VITAMINS.

	B <sub>1</sub>	B <sub>2</sub>	P.P	B <sub>6</sub>	C.	P.
Chemical Name.	Aneurin	Riboflavin	Nicotinic acid.	Adernin, Pyridoxin.	Ascorbic Acid	Citrin.
Deficiency disease	Ber-beri. Neuritis	Lack of growth. Cataract. Neural degeneration.	Pellagra. Lack of growth.	Dermatitis. Muscular degeneration ? Grey hair	Scurvy.	Capillary fragility.
Has been synthesised	Yes.	Yes.	Yes.	Yes.	Yes.	No.
Best sources	Wheat germ, yeast, roast pork, eggs.	Yeast, kidney, eggs.	Yeast, liver, wheat germ.	Yeast, rice, bran.	Rose hips, black and red currants, lemons, oranges, green vegetables, tomatoes.	Lemons.

## CHAPTER XVIII

### CHEMISTRY OF PHOTOGRAPHY

As mentioned in Chapter XII, the basis of photography lies in the rather unusual property of silver salts being affected by light. Sensitivity to light is not confined to silver salts, but this metal has been found to have this useful property to an extent which renders it of the greatest practical importance. Very briefly, it may be stated that plates and films are coated with a creamy mixture of silver bromide and gelatine, prepared in the dark by mixing silver nitrate solution containing gelatine with potassium bromide solution. Exposure of this creamy mixture, known as the emulsion, to light causes something to happen to the silver bromide which makes it capable of being reduced (developed) by suitable reducing agents, giving metallic silver in the places where the light has acted. Further, in those places where light has not acted, the emulsion does not develop. An image in black metallic silver is produced, and this is known as a negative because it is black where the original was light—in fact, its blackness is proportional to the brightness of the original object. This negative is fixed, or made permanent, by dissolving out of it the undeveloped silver bromide, thus leaving the black-and-white negative image with which we are all familiar. Fixing is done in a solution of hypo (sodium thiosulphate) in which silver bromide is soluble, but in which metallic silver is insoluble.

In order to transform the negative image into a reproduction of the original, or a positive, it must be printed. The most simple way of doing this is by exposing it to light in contact with another piece of light-sensitive material such as printing paper, which will be affected

by light in just the same way as was the first emulsion in making the negative. Thus the black parts of the negative will shield the printing-paper from the light, the clear parts will allow the light to act fully, and the areas which let some light through will partially affect the paper.

The printing paper can be of two kinds: it may be "print-out paper" in which a visible image is produced by the action of daylight and which needs no developing, or it is nowadays more usual to use what is known as gaslight or bromide paper, which forms no visible image (just like the film or plate in the camera) until it is developed. In either case the printed image must be rendered permanent, or fixed, in the same way as a negative.

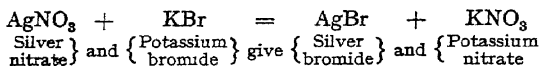
Many of the stages in the production of photographs are of considerable interest chemically, so that a more detailed account of these processes will now be given, and at the same time some of the gaps will be filled in.

In the first place, the film or plate is placed in a light-tight box, known as a camera, in which there is some device for holding it flat, and opposite to it is the lens which serves to project an image of the object to be photographed on to the film or plate. Usually, built into the front of the camera close to the lens, is a shutter which uncovers the lens mechanically, thus exposing the light-sensitive plate or film momentarily to the object, an image of which is thrown on to its surface by the lens. No visible effect of this exposure to light can be detected, but its results will be referred to again later.

As already mentioned, the light-sensitive material used in the camera may be in the form of either plates or films, but both carry the same emulsion of silver bromide and gelatine, so that it is principally a matter of choice which is nowadays used. Glass plates have the advantage of rigidity, and they are made from selected glass, free from irregularities and bubbles, and are most carefully cleaned before being coated with the emulsion.

Films are usually made of celluloid, except in the case of amateur cine-films, which are made of "safety" film, being composed of cellulose acetate which does not burn so readily as celluloid. The emulsion is coated on to the plate or film after a layer of plain gelatine has first been coated, in order to ensure proper adhesion of the emulsion to the base.

The emulsion is made under very carefully controlled conditions; the silver nitrate is of a very high standard of purity, the gelatine is tested and, as far as possible, standardised so as to try to ensure that successive batches of emulsion have properties which are as nearly alike as possible. If silver nitrate solution is added to potassium bromide solution, a white, curdy precipitate of silver bromide is produced, as may be shown by the equation :—



Normally, this precipitate, which is fairly heavy, falls to the bottom of the vessel, leaving the solution above it quite clear. If, instead of water, the two substances are dissolved in weak gelatine solution, the precipitate formed on adding one to the other no longer settles, but forms a milky solution, called an emulsion, in which the particles of silver bromide are held suspended. In making the emulsion, a slight excess of potassium bromide is added in order to precipitate all the silver; it is customary also to have present a small amount of potassium iodide, which forms a correspondingly small quantity of insoluble silver iodide in the emulsion. This substance has the effect of increasing its sensitivity. The emulsion is allowed to stand for some time, during which it is kept warm and matured; small quantities of ammonia may be added. This maturing action, known as ripening, further increases the sensitivity, and during its action the grains of silver bromide, which are minute

crystals of various sizes, grow; the large grains increase in size at the expense of the smaller ones. Before the emulsion is used it is cut up into small shreds and thoroughly washed, in order to remove from it all soluble salts such as excess of potassium bromide or nitrate. After washing, and whilst making ready for coating on to the plates or films, substances called sensitisers are added to it in order to increase its general sensitivity and also to make it capable of "seeing" colours. Ordinary or non-colour-sensitive emulsion is only able to "see" blue and violet light, and for this reason it may be examined and developed in the light from a red lamp, to which it is practically insensitive.

Coating is done by means of special machinery, and when the material is dry—a process which takes some time—it is cut up into the required sizes. Plates are cut and packed, films are slit and spooled. The sensitisers which are added to the emulsion before it is coated are complex organic compounds, and are actually dyestuffs having special properties; they are used in extremely small quantities. A large number of these sensitising dyes are now known, and by incorporating them in the emulsion it is possible to make it sensitive to practically any region of the spectrum, visible or invisible. There are also traces of compounds in the gelatine itself, which have the effect of making the emulsion more generally sensitive; they play their part during the time of ripening.

One such compound, traces of which have a powerful effect upon sensitivity, is one of the "mustard oils", allyl iso-thiocyanate,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}\cdot\text{S}$ . It has further been shown that the grouping  $\text{-NH-CS-N=}$  is responsible for this action.

In the camera the image of the thing seen by the lens is thrown momentarily upon the surface of the emulsion by the action of the opening and closing of the shutter. As already mentioned, nothing can be seen to result from the action of this light, but that something has happened is one of the basic principles of photography. An im-

pression known as the "latent image" is made in the silver bromide emulsion, some parts of which receive more light than others. Not much is known with certainty about the latent image, but it is believed that those crystals of silver bromide which are struck by light are rendered developable by the formation, somewhere inside them, of a minute speck of metallic silver, much too small to be seen or measured in any way, but nevertheless believed to be formed.

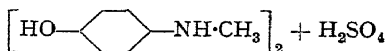
The next stage after exposure is development. As was mentioned earlier, development is the reduction, by means of a suitable reducing agent, of those particles of silver bromide which have been affected by light; the latent image is transformed into a visible image. The reducing agent must not be too strong, or else it will not differentiate between the exposed and unexposed grains, and it must not be too weak, or else only those parts of the latent image which are most heavily exposed will be reduced and the lighter parts will escape. Experience has shown that there are certain compounds—for example, hydroquinone or pyrogallol—which develop very well in the presence of an alkali, such as sodium carbonate. These are organic compounds, derivatives of benzene, but there are inorganic substances which act just as well, such as freshly prepared ferrous oxalate, but they are no longer of practical importance.

Organic developing agents are almost exclusively used nowadays; a very popular developing mixture is known as "metol-hydroquinone", which consists of a solution containing the substances, hydroquinone, metol, sodium carbonate, sodium sulphite, and potassium bromide. Most of the organic developing agents belong to the class of phenols (hydroxybenzenes), amines (aminobenzenes), and aminophenols. Hydroquinone, for example, is dihydroxybenzene:—





and metol is the trade name for methyl-*p*-aminophenol-sulphate :—



Another well-known developing agent is *p*-aminophenol,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ . It is the main constituent of many of the popular "single-solution" developers, such as "Azol", "Certinal", "Rodinal" and others.

Developing agents which are not so energetic as those already mentioned are used for producing negatives of "fine grain". Foremost amongst these is *p*-phenylenediamine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ . The developer known as "Glycin" is, in reality, *p*-hydroxyphenyl-aminoacetic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$  (cf. Glycine, p. 182).

As most of these developing agents only work in alkaline solution, there is sodium carbonate present, and this is believed to form a loose compound with the reducing agent in the form of a sodium salt. The alkali is often called the accelerator, as without it development would, at the best, proceed very slowly. As the alkaline solution of the developing agent by itself is a reducing agent, it is liable to be oxidised by the oxygen of the air; this is prevented by the addition of a preservative which is usually sodium sulphite, itself more readily oxidisable than the developing substance, thus keeping it free from aerial oxidation. Lastly, the potassium bromide is added as a restrainer in order to prevent the too-energetic action of the developing agent, which might otherwise develop unexposed grains of silver, thus causing an all-over blackening of the negative known as "fog".

When development has proceeded as far as desired, the negative is removed from the developing solution and placed in the fixing-bath. The essential constituent of this solution is "hypo" or sodium thiosulphate. The undeveloped silver bromide dissolves in this solution, and leaves the negative free from milky character characteristic of the emulsion. The hypo first transforms the emulsion

into a complex silver salt, which is not soluble in water, but is soluble in an excess of hypo, in which form it is removed from the gelatine. It is therefore good practice to leave the negative fixing for twice the length of time necessary to remove the last traces of milkiness; this ensures that the silver is completely removed as well as dissolved, a precaution necessary if good keeping quality is required in the negatives.

The fixing-bath often contains substances for hardening the gelatine; one such substance is alum, and this, in combination with acetic acid and sodium sulphite, gives what is known as an acid-hardening fixing-bath. The presence of the acid ensures that alkali carried over from the developer in the gelatine emulsion is neutralised, and so prevents staining. The object of hardening the gelatine is to prevent accidental damage to it while it is in its wet, soft state; in hot weather it becomes softer still, and may even melt completely and become detached from the plate or film. The actual effect of alum on gelatine is to tan it in the same way as leather is tanned; its chemical composition is actually changed, as is shown by the fact that it no longer melts so readily.

After fixing is complete the negative must be thoroughly washed, in order to remove from it as much of the hypo as possible. This substance, if allowed to remain in the gelatine, would ultimately decompose, and consequently adversely affect the keeping qualities of the finished negative. Washing should be carried out in a constant stream of cold running water, and if this is done, about 20 minutes suffices to remove practically every trace of hypo. If water is for any reason scarce, then quite small quantities of fresh water can be used in the form of about six successive changes; although this may take a little longer and be a good deal more trouble than the running-water method, it is perfectly effective and very economical when water cannot be readily obtained. Strange though it may appear, salt-water is most effective in removing hypo.

The last stage in the production of a negative is that of drying. This presents few difficulties, except that it may take rather a long time. If for any reason negatives are required quickly, they can be dried by bathing them in three or four changes of methylated spirit; this removes the surplus water and evaporates readily.

The finished negative must now be printed, and this is usually done on paper. Broadly speaking, there are three classes of printing paper—namely, gaslight, bromide, and print-out paper (P.O.P.). All of these consist of a paper base on to which is coated a very thin layer of emulsion. The base is carefully prepared, and usually carries a baryta coating which gives it an added whiteness. Over this coating is a very thin layer of gelatine, and over this gelatine layer is the emulsion itself. Gaslight and bromide papers are very similar; they differ only in the chemical composition of their emulsions. Gaslight paper is coated with a silver chloride emulsion, whilst bromide paper, as its name implies, carries an emulsion of silver bromide. These emulsions are prepared in a way very similar to those used in coating plates and films, but are very much less sensitive. Prints are made by placing the emulsion of the negative in close contact with the sensitive emulsion on the paper and exposing the paper, thus covered by the negative, to the light of, for example, an electric lamp. Gaslight papers are very much less sensitive to light than bromide papers, and therefore, as their name suggests, they may be handled in ordinary artificial light, providing this does not shine too strongly on to the sensitive surface. Exposure necessary for gaslight paper must therefore be relatively long, and a fairly bright light must be used. Bromide papers, on the other hand, are very much more sensitive, and they can only be used in a suitable dark-room which is illuminated by red or orange lamps. The exposed print, whether it be on gaslight or bromide paper, must be developed in just the same way as the negative was developed after exposure in the camera.

Similarly, when development is complete, it is fixed and then thoroughly washed. The chemical operations in all these processes are just the same as in negative making.

Another very popular method of printing involves the use of print-out paper. In this process, as the name suggests, the image is visible, and increases in density as the exposure proceeds. Most people are familiar with what happens when a piece of P.O.P. is placed in a printing-frame behind a negative and exposed to sunlight. The image gradually appears in a reddish colour, and before it becomes too dark the paper is removed; all that is necessary after this is to fix the image in plain hypo. Print-out papers are coated with an emulsion containing silver chloride together with citrate, tartrate, or oxalate of silver in the presence of an excess of silver nitrate; these combined cause the silver image to print out darkly under the influence of light. The fact that the image so produced is reddish in colour is due to the formation of silver in a more finely divided state than is yielded by the development of either gaslight or bromide emulsions. As the reddish colour of the P.O.P. image is not particularly pleasant, it is usual to tone the prints in order to make them more of a sepia colour. This is generally done by means of a solution containing gold chloride, and its effect is partly to replace the silver by metallic gold, and thus give the print a somewhat "cooler" tone. Print-out papers of the "self-toning" variety are nowadays very popular, and these actually contain the necessary gold combined in their emulsion so that toning takes place automatically as fixing proceeds.

It is also customary to turn black-and-white gas-light or bromide prints into images of various colours, the most popular of which is sepia. This latter process is known as sulphide toning, and in it the black silver image is transformed into brown silver sulphide; the method is as follows :—

The print is first placed in what is known as a bleaching

solution. This consists of a mixture of potassium bromide and a weak oxidising agent such as potassium ferricyanide. The effect of this solution is to transform the silver back into silver bromide, in which form it is more readily treated than if it were still in the form of the metal. When bleaching is complete, the print is almost white and the image on it is faintly cream in colour. The sepia image is produced by immersing this bleached print, after thorough washing, in a dilute solution of sodium sulphide, which transforms the white silver bromide into brown silver sulphide. After thorough washing the print is dried and the image of silver sulphide is extremely permanent.

In addition to after treatment to prints, it may sometimes be necessary to subject negatives to certain processes of "Correction", in order that prints of better quality may be obtained from them. The most usual of these after-processes are intensification and reduction. Intensification consists of adding something to the silver image in order to strengthen it and increase its density or contrast, whilst reduction is the converse process, in which the density or contrast of the silver image is reduced. In the first of these processes intensification is most commonly carried out by adding either mercury or chromium to the image. Other metals, such as uranium, can also be used, but the two of the most practical importance are mercury and chromium. When the negative is intensified with mercury, it is only necessary to immerse it first of all in a solution of mercuric chloride; the black image gradually bleaches out to form a double salt containing silver and mercury, and this is washed briefly with very dilute hydrochloric acid, which prevents the mercury from combining with the gelatine. The image is most simply blackened by immersing it in a very dilute solution of ammonia, the resulting compound being a complex one containing both mercury and silver, but having a greater density than the original silver image.

When intensifying with chromium, the silver image is bleached first of all with a solution comprising potassium dichromate and hydrochloric acid; this converts the silver into yellow silver chloride, and also adds to it a chromium compound. Bleaching is followed by washing, which removes all soluble salts, and then the negative is re-developed in an ordinary developer, in order to give an image of increased contrast. The process may be repeated should still greater intensification be required.

As mentioned previously, the process of reduction is the direct opposite to that of intensification, but, curiously enough, although the process is one in which the density of the negative is reduced, the chemical method of doing this is one involving the principle of oxidation. Briefly, the best-known reducer is a simple mixture of potassium ferricyanide and hypo; it must be freshly prepared and quickly used, as it does not keep, but in its action the silver image is converted into silver ferri-cyanide, which immediately dissolves in the hypo, thus causing a loss in density. Another very efficient reducing agent is a solution of iodine in potassium cyanide. Here the iodine combines directly with the silver to give silver iodide, which is readily soluble in potassium cyanide solution. Incidentally, it is interesting to recall that potassium cyanide solution was used as a fixing-bath in the early days of photography before the properties of the much better and much less harmful substance hypo were fully appreciated. Another simple reducing solution consists of potassium permanganate and sulphuric acid; the powerful oxidising properties of this mixture are well known, and when it acts on the negative, the silver is removed in the form of silver sulphate. As permanganate often produces a troublesome brown stain, it is wise to fix the negative in plain hypo solution, in order to remove the stain, after which it must be thoroughly washed.

A branch of photography which grows in importance every day is that of the production of photographs in

natural colours. The two most important spheres of application of any process of colour photography are in the cinema on the one hand and the printing industry on the other. In the cinema some form of colour photograph must be produced which is suitable for projection on to a screen; this is generally described as a transparency. On the other hand, for printing, some means must be found of transferring the coloured image on to paper. Colour transparencies have been of practical importance for a much longer time than prints on paper and, from the point of view of the amateur, are both simpler to understand as well as easier to produce. Broadly speaking, colour transparencies may be divided into two general classes: those produced by the additive method, and those in which the subtractive method is employed. In the additive method the three primary colours, red, green and blue, are used, and from them all intermediate colours are obtained by a process of addition. On the other hand, in the subtractive method the colours are revealed in the opposite way by the use of three colours which are the complimentary ones to the three primaries—namely, yellow, blue-green, and magenta. Subtractive processes are of increasing importance nowadays, both in the production of transparencies as well as colour prints, but amateur colour photography is generally carried out by using one of the additive methods, so that it is of more general interest to describe one of these in some detail. Some of the earliest transparencies were made by the Autochrome process, and a typical modern representative of this method is known as Dufaycolor.

A brief outline of colour photography by the additive process is of some interest chemically. The colour plate or film consists of an emulsion sensitive to all the colours of the spectrum (*i.e.*, panchromatic), in front of which is a screen made up of particles dyed red, green, and blue. This screen may be formed in a variety of ways, and gives rise to the other name for the method of additive colour

photography known as Screen-plate Colour Photography. In the Autochrome the screen is made up of myriads of dyed starch grains, whilst the Dufaycolor screen is a series of very fine-ruled red, green, and blue lines.

In the camera the colour plate or film is exposed to the action of light through this colour screen, and every part of the image is broken up into minute patches of colour corresponding to the three colours in the screen. The effect is exactly that of photographing through an immense number of red, green, and blue filters simultaneously, with the result that light reflected, say, from a red object will pass through the red elements of the colour screen, but will not pass through the green and blue elements; similarly a green object will be recorded on those parts of the emulsion which lie behind green colour elements but not behind red or blue, and in a like manner blue objects will also impress themselves on those parts of the emulsion which lie behind blue colour elements. When the colour of the original is made up from some mixture of red and blue, or blue and green, or red and green, the emulsion behind these pairs of colour elements will be correspondingly partially effected. Let us now suppose that the colour plate is developed in the usual way. The result will be the familiar negative image, but since this image is negative—*i.e.*, its darkest parts corresponding to those which were brightest in the original—its colours will be exactly complementary to those of the original. This negative image must therefore be made into what is known as a positive, which is exactly what is seen when a print is made on paper or in the form of a lantern slide or transparency. Instead of fixing the negative after development, it is rinsed and placed in what is known as a reversing-bath, which consists of a mixture of potassium dichromate and sulphuric acid. This solution dissolves out the black metallic silver which has been formed as a result of development, but leaves untouched the unexposed and consequently undeveloped silver bromide; its action is



therefore the opposite to that of the fixing-bath, which dissolves out the silver bromide, leaving the metallic silver unchanged. If the resulting image is held up to the light, it will be seen to show as a weak positive image made of creamy-white silver bromide, so that the next stage obviously is to make this image more intense, and this is done by first of all exposing it to ordinary diffused light, and then developing it. When this is done, the silver bromide is entirely changed to metallic silver, and a positive image of the original scene is produced. In this image those parts which originally lay behind, say, the red elements of the colour screen will be transparent, and so red light will be seen through them; blue light will be seen through those parts behind the blue elements, and similarly for the green elements. Thus the original scene is transformed into its component parts of red, green, and blue light. White light is produced by mixing equal proportions of red, green, and blue; yellow colours will be represented by mixing the red and green elements, whilst purple and violet tints will result from mixing the blue and red elements. By reason of the fact that the three colours in the elements of the colour screen must be added together in order to produce white light, the process has received the name of that of additive colour photography.

The other general group of colour photographic processes is that known as the subtractive process, which includes the two relatively recent systems produced by Agfa and Kodak, known respectively as Agfacolor and Kodachrome. The film in both these processes is made up of a number of light-sensitive layers superimposed one on the other with extremely thin colour-filter-layers in between. In the Agfa process, in addition to the sensitive emulsion there are extra chemicals mixed with these emulsions, which, when development takes place, will combine with a certain constituent of the developer to produce three colours, one in each layer, of intensity corresponding to the amount of silver image formed on

development. Instead of, as in the additive process, being red, green, and blue, these colours are their complementaries—namely, yellow, blue-green, and magenta—so that when added together they produce black instead of white, and the various colours are produced by removing one or more of the three colour layers. The principle of removing the colours gives rise to the general term subtractive process. The results produced by the Kodak process are strongly similar to the Agfacolor method, but the treatment of the film after exposure is considerably more complicated, and cannot be even briefly explained here. It should, however, be mentioned that in both processes the final image contains no silver whatever, but is made up purely of layers of dye in the gelatine, the silver having been dissolved during the course of processing.

So far we have considered briefly the production of transparencies or colour photographs which must be held up to the light in order to be viewed. The natural goal to which photographic technicians are working is the production of prints in full colours, and it is on this branch of colour photography that more time and money have been spent (and, for the most part, wasted) than on probably any other photographic process. This must not be taken to mean that good colour-prints cannot be produced. Such a statement is far from being the truth, but colour-prints are still very costly in comparison with the familiar black-and-white photographs, their cost being somewhere in the neighbourhood of at least ten times as much.

The general principle at present in use is to obtain what are called colour-separation negatives of the scene to be photographed, and from these negatives to build up a print by the subtractive process, using pigments on a paper base. Three negatives are made using a red, green, and blue filter, respectively, in order to record the red, green, and blue components of the subject. From these negatives prints are made and, since the print is

in each case the positive counterpart of the negative, they will be records of the colours complementary to those of the filters through which the negatives were made. Thus the red filter negative will give a print showing the blue-green colour content; the print from the blue filter negative will indicate the yellow content, whilst from the green filter negative the magenta component is recorded. If these three positives or prints from the negatives are superimposed, they will together reproduce the accurate colour representation of the original scene, and this is done by arranging things so that the coloured images can be stripped from their bases and placed one on top of another, in register, on a single support. It will be seen that there are any number of problems to be solved, the first of which is that of getting yellow, blue-green, and magenta pigments which are exactly complementary to the blue, red, and green filters used in exposure; the next difficulty is that of registering the three coloured images so that their edges do not overlap and consequently give coloured fringes in different parts of the picture, and last, but by no means least, there is the problem of obtaining reproducible results, so that when a batch of colour prints is made they are all of identical quality. These problems are being vigorously attacked and steadily solved by the work of many chemists and photographers, so that the day cannot now be far distant when we shall be able to obtain prints in accurate natural colours at very nearly as cheap a rate as we now obtain our black-and-white photographs.

## CHAPTER XIX

### CLASSIFICATION OF THE ELEMENTS

THE idea of the relative weights of the atoms of the elements has been outlined in Chapter I and a complete table of the Atomic Weights of the known elements is given on p. 236.

Up till now, our discussion of the chemistry of these elements has consisted, in the main, of a large mass of apparently unrelated facts; in places, family resemblances between certain sets of elements and their compounds have been brought out in passing, but the underlying system is far from being either obvious or complete.

We now propose to give, in the briefest outline, some of the facts which have helped to place the study of inorganic chemistry on a sound and systematic basis. The study is an interesting one, and serves as an example of how a vast mass of evidence, derived from the experimental labours of numerous chemists over a period of many years, has been built up into a lasting edifice. With its aid, many hitherto unknown elements have been discovered, and much of the recent development of atomic physics has been rendered possible.

Once a system of Atomic Weights had been agreed upon, and those relative weights carefully and accurately determined by experiment, it became evident that there was a strong, family resemblance in general chemical properties as well as some arithmetical ratio to be found in certain groups of elements. For example:—

Element.	At. wt.	Diff.	Element.	At. wt.	Diff.	Element	At. wt.	Diff.
Li	7		Ca	40		S	32	
Na	23	16	Sr	88	48	Se	79	47
K	39	16	Ba	137	49	Te	127	48

Each of these three groups of kindred elements can be seen to show a common difference between the atomic weights of successive members. These groups are known as "Döbereiner's Triads" (1817).

Somewhat later on, Newlands (1865) made a rather more striking observation, based on more complete data than Döbereiner had in his possession. What he said was: "If the elements are arranged in the order of their equivalents, with a few slight transpositions (see table), it will be observed that elements belonging to the same group usually appear on the same horizontal line:—

H (1)	F (8)	Cl (15)	$\begin{smallmatrix} \text{Co} \\ \text{Ni} \end{smallmatrix} \}$ (22)	Br (29)	Pd (36)	I (42)	$\begin{smallmatrix} \text{Pt} \\ \text{Ir} \end{smallmatrix} \}$ (50)
Li (2)	Na (9)	K (16)	Cu (23)	Rb (30)	Ag (37)	Cs (44)	Tl (53)
Gi (3)	Mg (10)	Ca (17)	Zn (25)	Sr (31)	Cd (38)	$\begin{smallmatrix} \text{Ba} \\ \text{V} \end{smallmatrix} \}$ (45)	Pb (54)
B (4)	Al (11)	Cr (19)	$\begin{smallmatrix} \text{Ce} \\ \text{La} \end{smallmatrix} \}$ (24)	Y (24)	U (40)	Ta (46)	Th (56)
C (5)	Si (12)	Ti (18)	In (26)	Zr (32)	Sn (39)	W (47)	Hg (52)
N (6)	P (13)	Mn (20)	As (27)	$\begin{smallmatrix} \text{Di} \\ \text{Mo} \end{smallmatrix} \}$ (34)	Sb (41)	Nb (48)	Bi (55)
O (7)	S (14)	Fe (21)	Se (28)	$\begin{smallmatrix} \text{Ro} \\ \text{Ru} \end{smallmatrix} \}$ (35)	Te (43)	Au (49)	Os (51)

"It will be seen that the numbers of analogous elements generally differ by either 7 or some multiple of 7; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the N group, between N and P there are seven elements; between P and As fourteen; between As and Sb fourteen; and lastly, between Sb and Bi, fourteen also." Newlands adds: "This peculiar relationship I propose to provisionally term the 'Law of Octaves'."

Next, a Russian chemist named Mendeleev (1869) proposed a "periodic table"; let us look at his arrangement and the evidence on which he based it (see table, p. 228).

He clearly recognised that the elements, when arranged in order of their atomic weights, showed a periodic change in properties; chemically analogous elements had atomic weights either closely in agreement or differing

Row.	Group I. $R_2O$ .	Group II. $RO$ .	Group III. $R_2O_3$ .	Group IV. $RH_4/RO_2$ .	Group V. $RH_3/R_2O_5$ .	Group VI. $RH_2/RO_3$ .	Group VII. $RH/R_2O_7$ .	Group VIII. $RO_4$
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	—*	Ti	V	Cr	Mn	Fe, Co, Ni, Cu.
5	(Cu)	Zn	—*	—*	As	Se	Br	
6	Rb	Sr	Yt	Zr	Nb	Mo	—	Ru, Rh, Pd, Ag.
7	(Ag)	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	D <sub>1</sub>	Ce	—	—	—	— —
9	—	—	—	—	—	—	—	
10	—	—	Er	La	Ta	W	—	Os, Ir, Pt, Au.
11	(Au)	Hg	Tl		Pb	Bi	—	
12	—	—	—	Th	—	U	—	— —

by equal amounts (cf. Döbereiner's Triads). Two pairs of elements caused some difficulty to Mendeleev; they were Te and I and Co and Ni. Chemical properties made it obvious in which order and in which groups they should appear, but considerations of Atomic Weight made them appear exceptions to the rule.

Amongst the numerous points advanced by Mendeleev in support of his table were the gradual increase in valency, as exemplified by the formation of oxides and hydrides, on passing from left to right, and also a steady change in general properties, from strongly electropositive (base-forming) through the amphoteric stage to strongly electronegative (acid-forming).

These, and other characteristic properties, which showed such marked periodicity, enabled him to be very sure that: (i) there were unfilled gaps in his table, (ii) the elements needed to fill those gaps would have certain predictable chemical and physical properties.

In several instances, he was able to forecast with astonishing accuracy the outstanding properties of the missing elements, and was even able to indicate where a search should be made for sources of these hitherto undiscovered elements.

For example, between Ca and Ti is a gap in Group III, and also there are two gaps between Zn and As in Groups III and IV, respectively (marked \* in Table). On account of analogies with foregoing elements he provisionally named these missing elements "eka-boron", "eka-aluminium" and "eka-silicon", respectively. From the regularities of the atomic weights of the known elements, he was able to predict the atomic weights of missing elements and, from their positions in his table, Mendeleev was able to predict their properties.

These predictions were brilliantly verified by the discovery of Scandium (1897), Gallium (1875) and Germanium (1886). As an example, let us look at a comparison of the predicted and observed properties of Germanium ("eka-silicon").

<i>Eka-silicon</i> , Es (1871)	<i>Germanium</i> , Ge (1886).
Atomic weight 72.	Atomic weight 72.6.
Density 5.5	Density 5.47.
Colour: dirty grey, giving white powder of $\text{EsO}_2$ on calcination.	Element is greyish-white metal, giving white $\text{GeO}_2$ on ignition.
Metal decomposes steam with difficulty.	Metal does not decompose water
Action of acids slight; that of alkalis more pronounced	Metal not attacked by $\text{HCl}$ ; dissolves in aqua regia.
	Aqueous $\text{KOH}$ no action but molten $\text{KOH}$ oxidises it with incandescence.
Element obtained by action of sodium on $\text{EsO}_2$ or $\text{K}_2\text{EsF}_6$	Element obtained by reduction of $\text{GeO}_2$ by carbon or of $\text{K}_2\text{GeF}_6$ by sodium.
Oxide $\text{EsO}_2$ refractory; sp. gr. 4.7; basic properties less pronounced than $\text{TiO}_2$ or $\text{SnO}_2$ but more marked than $\text{SiO}_2$ .	Oxide $\text{GeO}_2$ refractory; sp. gr. 4.703; very feebly basic, although indications of oxy-salts are found.
Chloride $\text{EsCl}_4$ liquid, b.p. below $100^\circ$ , sp. gr. 1.9 at $0^\circ$ .	$\text{GeCl}_4$ liquid, b.p. $86.5^\circ$ , sp. gr. 1.887 at $18^\circ$ .

<i>Eka-silicon, Es (1871).</i>	<i>Germanium, Ge (1886).</i>
Fluoride $\text{EsF}_4$ not a gas.	$\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ , white crystalline solid
Will form organo-metallic compounds, <i>e.g.</i> :	
$\text{Es}(\text{C}_2\text{H}_5)_4$ , b.p. $160^\circ$ , sp. gr. 0.96.	$\text{Ge}(\text{C}_2\text{H}_5)_4$ , b.p. $160^\circ$ , sp. gr. slightly less than water.

A complete new group (Group O) was added to the table by Ramsay on the discovery of the rare or inert gases, of which some mention has been made on p. 60. Many of the gaps have also been filled in, leaving only two elements to be isolated.

On the basis of these sure foundations, laid over seventy years ago, let us now examine the Periodic Table of today (see p. 231). It will be seen that Mendeleev's last two long periods have been combined into a single period of thirty-two elements containing the rare earth elements.

An entire group of new elements is formed by the inert gases of Group O, one member of which bridges the gap between each halogen and the succeeding alkali metal. The table is not only completed by this group, but it has a profound significance in the development of the theories concerning the structure of the atom.

The whole of the periodic classification is seen to consist of two short periods of eight elements each, two long periods of eighteen elements and an extra-long period of thirty-two elements, with a final fragmentary period.

Elements of the first two (short) periods are typical; on passing from the electro-positive alkali metals to the electronegative halogens, the whole scale of chemical properties is passed through. Between the extremities just named there lie elements (B, C, N, etc.) which are neither markedly positive nor negative. In the following period of eighteen elements, there lie the electro-positive metals K and Ca (analogous to the type elements in the short groups) at the beginning, and at the end are As, Se, and Br. Between the two extremes is a new



atomic weight, and therefore with the position of the element in the periodic classification. In particular, it has been found that melting-point, volatility, malleability and coefficient of expansion vary periodically.

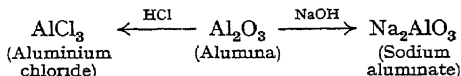
The best conductors of heat and electricity also fall into the same group. They will be seen to lie between those metals which are most easily fused and those which are least easily melted :—

High m.p.			Good conductors.	Low m.p.	
Fe	Co	Ni	Cu	Zn	Ga
Ru	Rh	Pd	Ag	Cd	In
Os	Ir	Pt	Au	Hg	Tl

Using the periodic table as a ground-base, we can trace the gradual change of chemical and physical properties as we pass from group to group (left to right or right to left) or up and down within the group. For example, the acidity of oxides increases from left to right, thus :—

	I.	II.	III.	IV.	V.	VI.	VII.
Oxides	Li <sub>2</sub> O Na <sub>2</sub> O	BeO MgO	B <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub> SiO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub> P <sub>2</sub> O <sub>5</sub>	— SO <sub>3</sub>	— (Mn <sub>2</sub> O <sub>7</sub> )
Basic ← ————— Amphoteric ————— → Acidic							

In groups I and II oxides are strong bases, in group III they show both properties, whilst groups IV, V, VI and VII show increasing acidity. Al<sub>2</sub>O<sub>3</sub> is "amphoteric", since it functions as either acid or base according to treatment :—



In addition, acidity of the oxides decreases with increasing atomic weight :—

Increasing acidity ↑	IV.	V.	VI.		VI.	Increasing basicity ↓
	CO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SO <sub>2</sub>	CrO <sub>3</sub>	
	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub> P <sub>2</sub> O <sub>3</sub>	SeO <sub>3</sub>	SeO <sub>2</sub>	MoO <sub>3</sub>	
	GeO <sub>2</sub>	As <sub>2</sub> O <sub>5</sub> As <sub>2</sub> O <sub>3</sub>	TeO <sub>3</sub>	TeO <sub>2</sub>	WO <sub>3</sub>	
	SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>5</sub> Sb <sub>2</sub> O <sub>3</sub>			UO <sub>3</sub>	
	PbO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>				

If a comparison is made, it will be observed that the atomic weight order of three pairs of elements in the table has been reversed. This course has been necessary despite exceedingly careful determination of the atomic weights of the elements in question. They are :—

A .	:	39.944	Te	:	127.61	Co	:	58.94
K .	:	39.096	I .	:	126.92	Ni	:	58.69

Just as Mendeleev found, in each case it is necessary to place the heavier element first. With the first two pairs (A and K ; Te and I) there is no cause for doubt, on chemical grounds, that the procedure is justified, since there is no chemical similarity at all between the pairs in question, and it is obvious into which group each should fall. Between Co and Ni there are grounds for uncertainty at first, but a careful examination of chemical properties confirms the arrangement.

From these considerations it clearly emerges that chemical properties are dependent not so much on atomic weight, but on the numerical position of the element in the periodic table. This position is called the Atomic Number and will be seen to be roughly proportional to the atomic weight. Thus, the properties of the elements are a periodic function of their atomic numbers. Although we have not space enough to say much more about it, the reader may be interested to learn that this idea of atomic number plays an important part in the speculations concerning the inner structure of

# INDEX

- ABSORPTION, 73
- Acetone, 147
- Acetylene, 85, 87, 143
- Acid, meaning, 32
- Acids, action on metals, 135
- Adrenalin, 196
- After-damp, 77, 142
- Air, analysis, 60
- Alcohols, 143
- Aldehydes, 146
- Aliphatic compounds, 149
- Alizarin, 94, 157
- Alkali, meaning, 33
- Allotropy, 74, 98, 114
- Alloy-steel, 130
- Alloys, 132
- Alum, 117
- Aluminium, 118, 135
- Amalgam, 132
- Amatol, 151
- Amines, 148
- Amino-acids, 182
- Ammonia, 45, 90
  - from air, 113
- Aneurin, 202
- Aniline, 93, 152
- Anthracene, 94, 154
- Anthracite, 76
- Antifebrin, 152
- Antiseptics, 108, 153
- Apparatus for experiments, xii
- Arc lamps, 87
- Aromatic compounds, 149
- Artificial diamonds, 75
  - gem-stones, 122
- Ascorbic acid, 204
- Aspirin, 152
- Atomic number, 234
  - weight, 20
  - weights, table, 27, 236
- Atoms, 18
- Avogadro's law, 21
- Bakelite, 165
- Basic, meaning, 32
- Benzene, 92, 149
- Beri-beri, 202
- Black-damp, 77
- Blast furnace, processes in, 129
- Blasting-gelatine, 112, 151
- Bleaching-powder, 107
- Blood, 191
- Brass, 133
- Bromide paper, 217
- Bromine, 108
- Bronze, 133
- Butter, 180
- Calciferol, 205
- Carbohydrates, composition, 176
  - definition, 174
  - digestion, 189
- Carbolic acid, 93, 150
- Carbon, 73
- Carbon monoxide, 79
- Carbonic acid gas, 76
- Carotene, 200
- Casein, 165
- Cast-iron, 130
- Catalyst, 96, 102, 113, 143, 144, 180, 232
- Cell, living, 182, 188
- Cellophane, 159
- Celluloid, 161
- Cellulose, 162, 178
- Cement and mortar, 120
- Chemical action, characters, 44
  - equations, 22, 47
- Chemicals, popular names, 39-43
- Chloramine-T, 153
- Chloral, 146
- Chlorine, 106
- Chloroform, 49, 142
- Chlorophyll, 64, 192
- Choke-damp, 77
- Clay, 117
- Coal, 76
  - gas, 83, 89
- Colloids, 52
- Colour photography, 221

- Combining power, 24  
 Combustion, 66  
 Compound, definition, 50  
 Condensation, 165  
 Copper, 134  
 Cordite, 112, 151  
 Corks, vii  
 Corrosion, of iron, 71  
 Creosote, 92  
 Crystalloids, 52  
  
 Davy lamp, 68, 85  
 Dehydration of food, 173  
 Deliquescence, 52  
 Detonators, 112  
 Development, photographic, 214  
 Dextrin, 44  
 Diamond, 74  
 Diamonds, industrial, 132  
 Disinfectants, 108  
 Displacement, 48  
 Distillation, 145  
 Döbereiner, 227  
 Double decomposition, 50  
 Drinking water, characters, 57  
 Dyes, 155  
 Dynamite, 112, 151  
  
 Earthenware, 121  
 Efflorescence, 52  
 Electric lamps, 86  
 Electrochemical series, 29, 55  
 Electrolysis, 54  
 Electroplating, 71  
 Element, definition, 20  
 Elements, common, table, 27  
 Emulsion, photographic, 210  
 Enzymes, 144, 178, 189  
 Essential oils, 146  
 Esters, 148  
 Ether, 145  
 Explosives, 112, 151  
  
 Fats, composition, 179  
     definition, 174  
     digestion, 190  
 Fatty acids, 148, 179  
 Fermentation, 144  
 Films, photographic, 211  
 Filters, x, 58  
  
 Fire-damp, 49, 83, 141  
 Fixing atmospheric nitrogen, 113  
     photographic, 215  
 Flame, structure, 84  
 Flash-point, 68  
 Flux, 129  
 Formalin, 146  
 Formulae, 22  
     structural, 23, 139  
 Fractional distillation, 92, 145  
 Fruit preserving, 101  
  
 Gaslight paper, 217  
 Gelatin, photographic, 213  
 Gelignite, 151  
 Germicides, 109  
 Glass, 121  
     organic, 163  
     tubing, vii  
 Glucose, 161, 177  
 Glycerin, 179  
 Glycogen, 178  
 Glyptal, 168  
 Gold, 17, 125, 127, 132  
 Granite, 122  
 Graphite, 74  
 Guncotton, 112, 151  
 Gunpowder, 45, 70  
  
 Hæmoglobin, 80, 192  
 Halogens, 107  
 Hardness of water, 56  
 Health-salts, 48, 79  
 Homologous series, 143  
 Hormones, 195  
 Hydrate, 38, 53  
 Hydrocarbons, 141  
 Hydrochloric acid, 105  
 Hydroquinone, 214  
 Hydrogen, 53, 103  
     nascent, 20  
 Hydroxide, 39, 53  
 Hypo, 37, 58, 107, 215  
  
 Incandescent gas mantle, 80, 86  
 Indicator, 33  
 Indigo, 155  
 Inert gases, 60, 230  
 Insulin, 191  
 Inulin, 178

- Intensifying negatives, 219  
 Iodine, 108  
 Iron, 127  
 Isomerism, 23, 139, 150  
  
 Jet, 76  
  
 Ketones, 147  
  
 Latent image, 214  
 Laughing gas, 113  
 Lignite, 76  
 Limelight, 85  
 Liquid air, 62  
 Litmus, 32  
  
 M & B 693, 154  
 Magnesium, 135  
 Maltose, 177  
 Margarine, 180  
 Marsh-gas, 49, 83, 141  
 Matches, 115  
 Mendeleev, 227  
 Mercury, 132  
 Metallic salts, 136  
 Metals, 124  
 Methane, 49, 141  
 Methylated spirit, 145  
 Metol, 215  
 Milk, 164, 177  
 Mineral salts, in foods, 185  
     water, 55  
 Moisture and chemical action,  
     71  
 Molecules, 18  
 Mordant, 118, 158  
 Muscles, 193  
  
 Naphthalene, 94, 154  
 Neon signs, 87  
 Newlands, 227  
 Nickel, 134  
 Nitrates, from air, 113  
     as fertilisers, 110  
 Nitric acid, 111  
     oxide, 112  
 Nitrogen, 61, 110  
     peroxide, 112  
 Nitroglycerin, 112, 151  
 Nitrous oxide, 113  
 Nordhausen acid, 102  
  
 Novocaine, 153  
 Nylon, 171  
  
 Octaves, Newlands', 227  
 Oil, from coal, 94  
 Oils and fats, 179  
 Ore deposits, 123  
 Ores, iron, 128  
     treatment, 129  
 Oxides, acidic and basic, 34  
 Oxy-acetylene welding, 88  
 Oxygen, 47, 61  
  
 Paintings, restoring, 99  
 Paraffins, 141  
 Peat, 75  
 Pellagra, 202  
 Periodic table, 227  
 Perspex, 164  
 Phenacetin, 152  
 Phosphoretted hydrogen, 114  
 Phosphorus, 114  
 Photography, 108, 136, 210  
 Picric acid, 151  
 Pig iron, 130  
 Plaster of Paris, 120  
 Plastics, 160  
 Plates, photographic, 211  
 Polymerisation, 163  
 Polypeptides, 170, 185  
 Print-out paper, 218  
 Proteins, composition, 181  
     definition, 175  
     digestion, 190  
 Protoplasm, 182  
 Pyrene, 142  
 Pyridoxine, 203  
 Pyroligneous acid, 148  
  
 Radicals, acid and basic, 31  
     alkyl, 143  
     organic, 140  
 Rayon, 163  
 Reducing negatives, 220  
 Refrigeration, 91  
 Respiration, 64  
 Riboflavin, 202  
 Rickets, 199  
 Rusting of iron, 71  
  
 Saccharin, 153

- Salt-cake, 105  
Salt, meaning, 33  
Scurvy, 199  
Seidlitz powder, 44  
Self-toning paper, 218  
Silica and Silicates, 119  
Silk, artificial, 169  
    natural, 170  
Silver, 127  
    bromide, 212  
Slag, 129  
Smelling salts, 91  
Soap, 181  
Soda-water, 79  
Solutions, 51  
Spontaneous combustion, 69  
Starch, 176  
Steel, 130  
Substitution products, 49  
Sucrose, 176  
Sugar, 176  
    in blood, 191  
Sulphides, 98  
    coloured, 46  
Sulphonamide drugs, 153  
Sulphur, 97  
    dioxide, 98, 100, 104  
Sulphuretted hydrogen, 99  
Sulphuric acid, 101  
Superphosphate, 114  
Symbols, 21  
Tar distillation, 91  
Test tubes, xi  
Therm, 80  
Thiamin, 202  
Thyroxin, 195  
T.N.T., 112, 151  
Toning photographic prints,  
    218  
Transitional elements, 232  
Triads, Dobereiner's, 227  
Tyrian purple, 156  
Urea, 24, 138, 166, 191  
Valency, 24  
Vat-dyeing, 156  
Viscose, 170  
Vitamins and health, 197  
Water, 51  
    of crystallisation, 38, 52  
    in food, 172  
        gas, 79  
        glass, 121  
        softeners, 56  
Welding, 88

